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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

WILLIAM FRANCIS, PH.D., F.L.S., F.R.A.S., F.C.S.

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No. CCCXVII.—January 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On new Compounds of Chloride of Cadmium.
By KARL VON HAUER*.

THE following chlorine compounds of cadmium were obtained with oxide of cadmium prepared by the calcination of the carbonate.

I. *Chlorobicadmiate of Barium.*—If solutions of 2 equivs. of chloride of barium and 1 equiv. of chloride of cadmium be mixed and evaporated to crystallization, chloride of barium first crystallizes; when further evaporated, the solution furnishes the monocadmiate already described, $BaCl+CdCl+4HO$.

It appears consequently that no basic compound with chloride of barium exists. The same salt is obtained, as already stated, by mixing solutions of equivalent proportions of the metallic chlorides. Lastly, when 1 equiv. of chloride of barium is mixed with 2 equivs. of chloride of cadmium, a portion of monocadmiate first crystallizes; but after the removal of this, the mother-liquor, when further evaporated, furnishes a salt the composition of which corresponds with the formula $BaCl+2CdCl+5HO$, and which is consequently a bicadmiate.

This, therefore, requires an excess of chloride of cadmium for its formation. It can, in fact, only be obtained pure at once by leaving for crystallization a solution which contains at least 3 equivs. of chloride of cadmium to 1 equiv. of chloride of barium. The salt forms octahedra and tetrahedra, part of which are turbid and part limpid. The crystals are hard and stable in the air, and may be brought to a considerable size, although this is very slowly effected. They frequently exhibit but little consistency, and readily break up into small hard fragments. Although the salt is produced from two very soluble compounds, it is itself rather difficult of solution. Analyses:—

Ba	20·88	20·78	20·66	1	=	68·5	20·65
Cd	33·83	34·09	34·31	2		112·0	33·76
Cl	31·88	32·27	32·36	3		106·2	32·01
HO	13·41	12·86	12·67	5		45·0	13·56

When the solution with the above equivalent proportions is rapidly evaporated until the commencement of crystallization, and then left to cool, there are formed for the most part stellate masses of crystals. The salt cannot be completely recrystallized. Thus if its solution be evaporated to the commencement of crystallization, only a portion recrystallizes undecomposed, whilst at the same time crystals of the salt $BaCl+CdCl+4HO$ are also produced. If, therefore, it be desired to recrystallize the salt, some chloride of cadmium must be added to the solution, because, as has already been stated, it is only formed in the presence of an excess of that salt. If the crystals be thrown into hot water, they become opake, and appear as though they had effloresced, a property which is exhibited by all the following salts under the same circumstances. Their solution takes place slowly.

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* See Chem. Gaz., Nov 15, 1855, p. 431.

When dried at 212° F., the crystals lose 6·59 per cent. of water, or nearly 2 atoms. It is several hours before the loss of weight at this temperature becomes constant. Between 293° and 302° F. 5·54 per cent. more water is driven off; this is also nearly 2 atoms. The last atom of water is only expelled at about 320° F. When more strongly heated, the salt fuses, like the monocadmiate, forming a clear colourless fluid, which on cooling does not solidify in a crystalline form.

If the salt, without being deprived of its water, be exposed at once to a high temperature, the expulsion of the water is accompanied by strong decrepitation of the crystals, which do not melt in their water of crystallization. The crystals, when heated to their melting-point, evolve fumes of chloride of cadmium. The fused mass is no longer completely soluble in water, but leaves a small residue, which however disappears on the addition of a few drops of an acid. At a temperature at which it begins to fuse, the salt also loses a part of its chlorine. The loss of weight of the salt thus heated amounted to 13·70 per cent., consequently a little more than the quantity of water contained in it. When the salt is slowly heated until it loses all its water, the form of the crystals is not destroyed.

II. *Chlorobicadmiate of Strontium.*—When a mixture of solutions of equal equivalents of these two chlorides are left to crystallize, a salt crystallizes out, which forms limpid, brilliant, and very long columns, which are pointed at the ends, and sometimes striated. When the quantity of the fluid is sufficient, the crystals attain a considerable size within a short time. The composition of the salt does not correspond with the proportions above given, but is that of a bicadmiate, with 7 atoms of water, according to the formula—

$$SrCl+2CdCl+7HO.$$

The salt is also obtained in the same way when proportions corresponding with this formula are employed. The salt is perfectly stable in dry air, but is somewhat deliquescent in moist air. Analyses:—

Sr	13·59	13·74	48·35	1	= 43·8	13·47
Cd	34·63	34·01		2	112·0	34·46
Cl	32·03	32·34	31·12	3	106·2	32·67
HO	19·75	19·91	19·53	7	63·0	19·38

The salt cannot be dried over sulphuric acid or chloride of calcium, from its efflorescing. It crystallizes unchanged from its aqueous solution. When dried at 212° F., it loses 5·05 per cent. of water, or 2 equivs.; between 267° and 276° F., 2·68 per cent., or a third atom; and when further heated to 338° F., 6·43 per cent., or a little more than 2 atoms; the two last atoms of water, however, are only driven off at a temperature of more than 356° F. When still more strongly heated, it melts, like the preceding salt, forming a clear colourless fluid, which on cooling forms a nacreous mass. By this means it also loses a part of its chlorine, for the fused mass, when dissolved in water, leaves a residue, which disappears on the addition of an acid. The salt, heated to its melting-point, showed on the average of two experiments a loss of weight of 20 per cent., consequently a few tenths per cent. more than its amount of water. During fusion vapours of chloride of cadmium are evolved, so that if this be long continued the loss of weight increases in proportion. If the salt be heated only until the loss of its water, it retains its crystalline form, and exhibits a strong lustre on its surfaces. The crystals thus dried dissolve in water without residue.

III. *Chlorobicadmiate of Calcium.*—This salt appears to require an excess of chloride of calcium for its formation. It is therefore best prepared by mixing a solution of 1½ equiv. with one of 2 equivs. of chloride of cadmium, and evaporating to crystallization. It forms shining columnar crystals, pointed at the extremities and grouped in a stellate form, which may be isomorphous with those of the strontium-salt. The salt is rather deliquescent and very soluble. For these two reasons it is rarely possible to obtain it by the spontaneous evaporation of the solution. But if the solution be concentrated by heat and then allowed to cool, the whole mass generally sets into a crystalline jelly consisting almost entirely of fine needles, which can only be freed with difficulty from the adherent mother-liquor. It must then be repeatedly pressed between blotting-paper, and afterwards completely dried over chloride of calcium. But if a moderately concentrated solution be left to spontaneous evaporation under a bell-glass over chloride of calcium, or under the air-pump, it is obtained in beautiful well-developed crystals. From the difference of their appearance it would appear that the crystals obtained in these two methods must have a different composition, but their analyses gave the same results. Thus the composition of both was found to be analogous to that of the strontium-salt, according to the formula $CaCl+2CdCl+7HO$.

When left too long over chloride of calcium, the crystals appear to lose some chemically-combined water, as they become dull on their faces. For the purpose of analysis, therefore, the fine acicular crystals were pressed between blotting-paper, and afterwards dried over caustic lime, but the large columnar crystals were dried at once by the latter means. They completely retained the lustre of their faces.

Analyses:—

Ca	6·83	6·97	1 =	20·0	6·64
Cd	36·58	36·45	2	112·0	37·18
Cl	35·79	35·22	3	106·2	35·26
HO	20·80	21·36	7	63·0	20·91

When heated to 212° F., the salt loses only an inconsiderable quantity of water; to deprive it of all its water requires nearly a red heat. The dehydrated salt dissolves in water like chloride of calcium, with evolution of heat; that containing water, on the contrary, produces refrigeration. Whilst in this respect the characteristic properties of chloride of calcium predominate, to a certain extent, the salt differs essentially from this in its behaviour when exposed to heat. Thus crystallized chloride of calcium melts below 212° F., and when more strongly heated loses its water with violent effervescence. Neither of these phænomena takes place with the double salt with chloride of cadmium; this does not melt in its water of crystallization, and it loses its water completely whilst still perfectly retaining its crystalline form. The crystals, when heated to redness after the expulsion of their water, fuse with evolution of vapours of chloride of cadmium. The fused crystals solidify into a gray amorphous mass, which in consequence of decomposition is but slightly soluble in water. The salt cannot be well recrystallized, but generally remains in the form of a white amorphous mass.

IV. *Chlorohemicadmiate of Calcium.*—A solution containing 2 equivs. of chloride of cadmium and 1 equiv. of chloride of calcium, concentrated by heat, deposits on cooling a quantity of the bicadmiate just described, in the form of fine needles. If these be removed from the mother-liquor and the latter again heated, large polyhedral crystals are produced, the composition of which is represented by the formula—

$$2CaCl + CdCl + 12HO.$$

The salt appears to require a considerable excess of chloride of calcium for its formation, as even with a proportion of 3 equivs. of the latter to 1 equiv. of chloride of cadmium, a small quantity of the bicadmiate is always first separated.

From their large amount of chloride of calcium the crystals are very deliquescent. They effloresce under the air-pump over sulphuric acid, but only after a long time. For the purpose of analysis they were dried in a bell-glass over chloride of calcium. Analyses:—

Ca	13·37	13·29	2 =	40·0	12·89
Cd	17·86	17·75	1	56·0	18·05
Cl	33·89	33·68	3	106·2	34·23
HO	34·88	35·28	12	108·0	34·81

Dried at 212° F., when it melts in its water of crystallization, which indeed takes place even at a lower temperature, it loses 17·95 per cent. of water=6 atoms; between 257° and 266° it loses 12·31 per cent., or 4 atoms, and the last 2 atoms between 302° and 311° F. The salt exhibits the essential properties of chloride of calcium, such as the tendency to attract water and deliquesce with it, to melt in its water of crystallization at a low temperature, the evolution of the water with strong frothing, the production of cold during the solution of the aquiferous crystals, and the evolution of heat in that of the fused mass. When more strongly heated, it fuses for the second time with partial decomposition, like all the other compounds already described.

V. *Chlorobicadmiate of Magnesium.*—This compound is obtained in the same manner, both when the two chlorides are mixed in equal proportions, and when 2 equivs. of chloride of cadmium are mixed with 1 equiv. of chloride of magnesium. Large, limpid, columnar crystals are formed, which may readily be brought to a length of more than an inch. In dry air the crystals are stable, but in moist air they deliquesce. When dried over sulphuric acid or chloride of calcium, they lose a great part of their water, and become quite opake. For analysis the salt was dried upon blotting-paper under the air-pump, by which no change is produced. The larger crystals generally contain mechanically-enclosed water, as their increase takes place very rapidly; they are consequently not suited for analysis. Analyses:—

Mg	3·73	3·50	1 =	12·0	3·54
Cd	33·48	32·93	2	112·0	33·11
Cl	31·22	30·64	3	106·2	31·40
HO	31·57	32·93	12	108·0	31·93

The salt may be recrystallized without decomposition. The crystals dissolve like those of chloride of magnesium, with production of considerable cold. Crystallization only takes place when the fluid is greatly concentrated, as the salt is very soluble. Its solubility is considerably increased by heat, so that a hot concentrated solution, which exhibits no trace of crystallization, often sets entirely on cooling into a solid mass, which consists entirely of fine acicular crystals.

When dried at 212° F., it loses 16·01 per cent., or 6 atoms of water. At a slightly higher temperature it fuses in its water of crystallization, and afterwards loses the latter; but in this case it behaves like ordinary chloride of magnesium, as simultaneously with the water a portion of the muriatic acid is evolved, so that the quantity of water cannot be determined from the loss of weight by heat. On this account also the mass remaining is but slightly soluble in water.

VI. *Chlorohemicadmiate of Magnesium.*—When a mixture of the aqueous solutions of 2 equivs. of chloride of magnesium and 1 equiv. of chloride of cadmium is strongly evaporated, large tabular crystals are deposited from it on cooling. Whilst in general the salts belonging to this group always require an excess of the basic metallic chloride for their formation, this is not the case with this salt. The salt is very soluble, and is deliquescent both in dry and moist air. The corresponding calcium-salt exhibits the same property in a still higher degree. Its composition corresponds with the formula—

$$2MgCl + CdCl + 12HO.$$

For analysis it was dried over chloride of calcium under the air-pump, no other mode of drying appearing sufficient. Analysis:—

Mg	8·26	2 =	24·0	8·15
Cd	19·34	1	56·0	19·03
Cl	35·42	3	106·2	36·09
HO	36·98	12	108·0	36·71

The crystals dried in the above manner, when exposed to a temperature of 212° F., lost only about 1 per cent. of water. When more strongly heated, they behaved like chloride of magnesium, and in general they exhibited the characteristic properties of the latter more prominently than the bicadmiate. In the crystallization of this and the preceding salt, the presence of free muriatic acid appears to be somewhat injurious.

VII. *Chlorobicadmiate of Manganese.*—Like the corresponding magnesium-salt, this was obtained by mixing 1 equiv. of chloride of manganese with 2 equivs. of chloride of cadmium. As it is very soluble, it crystallizes with some difficulty, and scarcely until the solution is brought to a syrupous consistence. The crystallization is best effected by leaving the strongly evaporated solution to further spontaneous evaporation in perfect quiet. It forms pale rose-coloured columns, which become almost white by repeated recrystallizations, like those of the magnesium-salt obtained in the same way. The crystals may be brought to a considerable size. In very dry air they effloresce at the surface, and consequently even when dried over chloride of calcium and sulphuric acid; in moist air they are deliquescent. They may however be kept in well-stopped vessels without exhibiting any change.

Their composition is analogous to that of the magnesium-salt, in accordance with the formula $MnCl + 2CdCl + 12HO$. Analyses:—

Mn	7·62	7·47	1 =	27·6	7·80
Cd	31·96	32·45	2	112·0	21·65
Cl	29·76	30·00	3	106·2	30·01
HO	30·66	30·08	12	108·0	30·53

When thrown into hot water, the crystals exhibit the same property as most of these salts, becoming opake and efflorescent in appearance. If the solution be evaporated for recrystallization, this does not take place on cooling, a gelatinous mass being deposited; but if a few drops of muriatic acid be added to the solution, the salt again crystallizes unchanged. Nevertheless this appears to have less influence upon the crystallization than the circumstance that the salt crystallizes more readily when the solution is left to spontaneous evaporation than when it is to be obtained by the cooling of a solution concentrated by heat.

When dried at 212° F., the crystals lose 24·79 per cent. of water, or nearly 10 atoms; they behave consequently exactly like the corresponding magnesium-salt. It loses the last 2 atoms a little above 320° F. When strongly heated at once, it decrepitates slightly, without melting in its water of crystallization, and after the loss of its water fuses at a heat approaching redness; it is thus rendered brown, when the air has access to it, from the formation of protoperoxide, whilst chloride of manganese and cadmium are partially volatilized. On cooling, it forms a shining crystalline mass.

When solutions of 2 equivs. of chloride of manganese and 1 equiv. of chloride of cadmium are mixed, and the fluid is concentrated, protochloride of manganese first crystallizes, and on further concentration the bicadmiate just described. It appears therefore that no hemicadmiate analogous to that of magnesium exists.

VIII. *Chlorobicadmiate of Iron.*—The solution of the two chlorides in equivalent proportions deposits large columnar crystals, which are very probably isomorphous with the two bicadmiates of magnesium and manganese, as their composition was shown to be the same, agreeing with the formula $FeCl+2CdCl+2HO$.

For the preparation of the salt, crystallized protochloride of iron was employed. This was obtained in the ordinary method by boiling an excess of metallic iron with muriatic acid, the air being excluded as much as possible; the solution, when sufficiently concentrated, was left to cool. The crystals were rapidly dried, and the proper quantity of them was dissolved in a hot concentrated solution of chloride of cadmium, and then placed in a gas-glass over chloride of calcium, and left to further evaporation.

The green fluid deposits crystals, which when taken out are nearly colourless, but soon afterwards become greenish, and finally yellowish. They effloresce rapidly over chloride of calcium and sulphuric acid. At ordinary temperatures they are neither deliquescent nor efflorescent, but gradually acquire an intense yellow colour.

For analysis the salt was rapidly freed, by repeated pressure between blotting-paper, from the adherent mother-liquor, and then completely dried over caustic lime. Analyses :—

Fe	8·52	8·15	1 =	28·0	7·90
Cd	30·60	31·79	2	112·0	31·62
Cl	30·00	30·39	3	106·2	29·98
HO	30·88	30·47	12	108·0	30·49

Even when moderately heated, the salt fuses in its water of crystallization; it then becomes dry, and exhibits a yellow colour; and when further heated with access of air, it becomes red from the formation of peroxide of iron. With the exception of its very slight deliquescenec, therefore, it behaves essentially like crystallized protochloride of iron.

IX. *Chlorobicadmiate of Cobalt.*—The formation of this salt appears to require the presence of an excess of protochloride of cobalt. It is most readily formed when about 1½ equiv. of that salt is mixed with 2 equivs. of chloride of cadmium, and the concentrated solution of the mixture is left to spontaneous evaporation in a moderately warm place. Crystallization rarely takes place on the cooling of a solution concentrated by heat. The salt crystallizes in beautiful large columns of the colour of protochloride of cobalt, and the form of the compounds of magnesium, manganese, and iron with 12 equivs. of water. Its composition is also the same as that of those salts, in accordance with the formula $CoCl+2CdCl+12HO$.

It is somewhat deliquescent in moist air, but stable in dry. When dried over sulphuric acid and chloride of calcium, it effloresces, and also over caustic lime, although only superficially and after a considerable time.

For the analysis, therefore, the desiccation was effected upon blotting-paper under the air-pump, as by this means it becomes perfectly dry without losing any chemically-combined water. The separation of the cobalt and cadmium was effected by means of sulphuretted hydrogen in the strongly acidified solution. After the sulphuretted hydrogen had been got rid of, the cobalt was precipitated by hydrate of potash. Analyses :—

Co	8·22	7·56	1 =	29·5	8·30
Cd	31·54	32·50	2	112·0	31·48
Cl	29·61	29·64	3	106·2	29·85
HO	30·63	30·30	12	108·0	30·36

When dried at 212° F., it loses 25·46 per cent., or 10 atoms of water, and the remaining 2 atoms between 302° and 311° F.; it is then of a blue colour. If the crystals be exposed directly to a somewhat higher temperature, they melt partially in their water of crystallization with a dark violet colour; after the loss of the water, the mass becomes solid, and forms a light bluish substance, like protochloride of cobalt evaporated to dryness. At a temperature near red heat it fuses again, and sublimes with partial decomposition, so that the residuary mass is but slightly soluble in water.

X. *Chlorobicadmiate of Nickel.*—This compound, like the preceding, also requires an excess of chloride of nickel, and is best obtained with the proportions given for the cobalt-salt. It forms large, dark green, columnar crystals, of the same form as those of the cobalt-salt. The composition agreed with the formula $NiCl+2CdCl+12HO$.

Like the cobalt-salt, it is readily soluble, and is best obtained when the solution is left to evaporate spontaneously at ordinary temperatures. Over chloride of calcium it effloresces completely, and becomes white. For analysis the crystals were dried over caustic lime. Analyses :—

Ni	8·54	8·71	1 =	29·6	8·32
Cd	31·33	31·25	2	112·0	31·47
Cl	29·66	30·16	3	106·2	29·84
HO	30·47	29·88	12	108·0	30·35

At 212° F. it loses 26·63 per cent., or about 10 atoms of water; the last 2 atoms go off between 320° and 329° F., consequently only at a higher temperature than in the analogous cobalt-salt.

If the crystals, immediately before their deprivation of water, be exposed to a somewhat higher temperature, they melt partially in their water of crystallization, and when dried then form a dingy yellow earthy mass, like the chloride of nickel obtained by evaporation, which gradually dissolves again in water with a green colour. If the application of heat be carried further, chlorine is driven off, and a partial decomposition takes place.

The crystals obtained cannot easily be recrystallized, as, like the cobalt-salt, they require for their formation the presence of an excess of protochloride of nickel; they cannot be readily obtained by the cooling of a hot saturated solution. But if crystals be placed in a saturated solution which contains no excess of protochloride of nickel, they undergo no alteration.

XI. *Chloromonocadmiate of Copper.*—From a solution containing the two chlorides in equal equivalents a salt is deposited, which forms fine shining columns united in tufts; its composition agrees with the formula $CuCl + CdCl + 4HO$.

The crystallization takes place with some difficulty, and not by evaporation by heat, as by this means the salt strongly effloresces. It is best obtained from a solution which contains no excess of acid by spontaneous evaporation at the ordinary temperature of a room. When the crystals are taken out of the mother-liquor, and as long as they are in the moist state, they appear green, but when dry they are of a blue colour. They cannot be dried over chloride of calcium, as they effloresce; in other respects the salt is stable in the air. For analysis it was dried over caustic lime. Analyses:—

Cu	16·66	15·67	1	=	31·7	16·29
Cd	28·49	29·29	1		56·0	28·79
Cl	35·75	36·24	2		70·8	36·40
HO	19·10	18·80	4		36·0	18·51

When heated, the salt does not melt in its water of crystallization; the water is driven off without the crystals losing their form. After the loss of their water they appear of a brown colour, and resemble dehydrated perchloride of copper. They only fuse when strongly heated after the expulsion of the water, forming a dark brown fluid, which is partly evaporated. The fused mass solidifies in a crystalline form, and has a grayish-brown colour.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xvii. p. 331.

Conversion of Oxide of Carbon into Formic Acid.

By M. Berthelot.

Oxide of carbon presents the same relation towards formic acid as olefiant gas towards alcohol; the two gases only differ from the corresponding compounds by the elements of water,—

$$C^2 H^2 O^4 = C^2 O^2 + 2HO.$$
$$C^4 H^6 O^2 = C^4 H^4 + 2HO.$$

Moreover, oxide of carbon may be obtained by treating formic acid with concentrated sulphuric acid, in the same manner as olefiant gas from alcohol.

These resemblances have led me to convert oxide of carbon into formic acid in the same manner that I effected the conversion of olefiant gas into alcohol, except that instead of producing the fixation of the elements of water by means of sulphuric acid, a substance adapted to combine with alcohol, I had recourse to potash, a substance capable of combining with formic acid.

I operated in the following manner:—10 grms. of potash, slightly moistened, were placed in a balloon containing half a litre, which was then filled with pure oxide of carbon* and sealed up. Ten or twelve of these balloons were then arranged in a water-bath, and heated for seventy hours to 212° F. The balloons were then opened over mercury, when it was found that a nearly complete vacuum had been produced; the carbonic oxide had been absorbed by the potash.

The contents of the balloons were dissolved in water, supersaturated with sulphuric acid, and distilled. The distilled product was treated with carbonate of lead, boiled, and filtered; the liquid on cooling deposited crystals of formiate of lead.

These crystals possessed the normal properties, reactions, and composition; they readily gave off pure oxide of carbon at 212° F., in the presence of concentrated sulphuric acid.—*Comptes Rendus*, Nov. 26, 1855, p. 955.

Researches on some new Phosphuretted Bases.

By MM. A. CAHOURS *and* A. W. HOFMANN.

In a paper by M. Paul Thenard (Comptes Rendus, xxi. p. 144, and xxv. p. 892), on the reciprocal action of hydrochloromethylic æther and phosphuret of calcium, that chemist announced the existence of several products corresponding to the different compounds which phosphorus forms with hydrogen, in which the latter element is replaced by equivalent quantities of methyle. More recently the discovery of stibæthyle by MM. Löwig and Schweitzer, and that of M. Hofmann relating to the compound ammonias, have shown that in ammonia and its analogues the hydrogen may be partially or wholly replaced by binary groups, such as methyle, æthyle, amyle, phenyle, &c., without depriving them of their basic properties; indeed, as regards the compounds of arsenic and antimony, these properties are considerably exalted by the introduction of the preceding radicals in place of hydrogen. On the other hand, the discovery of the tetramethylated and tetræthylated bases, &c. by M. Hofmann, and that of the corresponding bases of arsenic and antimony made simultaneously by MM. Cahours and Riche and by M. Landolt, show that we may go still further, and replace the 4 equivs. of hydrogen contained in ammonium by equivalent quantities of the alcoholic radicals, and that besides there exist arsenical and antimonial compounds corresponding with ammonium. The gap between the compounds of nitrogen and those of arsenic remained to be filled up; the study of the phosphuretted compounds appeared to promise a rich harvest of facts, and this induced the authors to undertake the experiments communicated in the present paper.

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* Prepared either by means of oxalic acid, or of a mixture of chalk an charcoal.

They first endeavoured to produce the phosphuretted compounds corresponding with ammonia and ammonium by a course similar to that followed by M. Thenard, substituting phosphuret of sodium for phosphuret of calcium; phosphuret of sodium is easily obtained by the direct combination of sodium and phosphorus. Hydriodomethylic æther was also substituted for hydrochloromethylic æther. The action is very brisk with the aid of heat, and inflammable and detonating products are formed, so that this mode of preparation is attended with danger, and complex products are obtained, the separation of which is only effected with great difficulty. The following compounds were formed:—

PMe^2, a liquid corresponding with cacodyle;

PMe^3, a liquid corresponding with stibæthyle and triæthylamine;

PMe^4I, a beautifully crystallized substance, corresponding with iodide of tetramethylammonium.

The difficulties attending this mode of preparation induced the authors to seek another, and they tried the mutual action of terchloride of phosphorus, PCl^3, and zincmethyle, zincæthyle, and zincamyle. When one of these compounds is placed in a U-tube, filled with carbonic acid, and vapours of terchloride of phosphorus are passed through it, the mass becomes strongly heated, and a viscous substance, which solidifies completely on cooling, is speedily formed. This solid mass is a compound of chloride of zinc with triphosphomethylamine, triphosphæthylamine, &c., according to the radical employed. These reactions are easily understood by the following equations:—

$$PCl^3+3(C^2H^3Zn)=3ClZn+P(C^2H^3)^3.$$
$$PCl^3+3(C^4H^5Zn)=3ClZn+P(C^4H^5)^3.$$
$$PCl^3+3(C^{10}H^{11}Zn)=3ClZn+P(C^{10}H^{11})^3.$$

When these compounds of chloride of zinc with the phosphuretted radicals are distilled with an excess of a solution of caustic potash, chloride of potassium and zincate of potash are formed and remain in the retort, and the distillates consist of volatile oils of a peculiar odour, which resembles that of the arseniuretted bases; they are endowed with very decided alkaline properties, and analysis shows them to be triphosphomethylamine, triphosphæthylamine, and triphosphamylamine. These bodies form crystallizable and very soluble salts with acids; with bichloride of platinum their muriates furnish very soluble compounds of an orange colour, which form beautiful crystals by slow evaporation.

Triphosphomethylamine, brought in contact with iodide of methyle, forms a solid matter, which is very soluble in alcohol, and which separates from this liquid on evaporation in the form of long white needles of the formula $P(C^2H^3)^4.I$. It is consequently iodide of tetraphosphomethylammonium.

Iodide of æthyle acts in the same manner, but less energetically, and furnishes a compound isomorphous with the preceding, represented by the formula $P(C^2H^3)^3(C^4H^5).I$.

With iodide of amyle, $P(C^2H^3)^3(C^{10}H^{11}).I$ is obtained.

Triphosphæthylamine, treated in the same way with the alcoholic radicals, gives—

$$P(C^4H^5)^3(C^2H^3).I,$$
$$P(C^4H^5)^4.I,$$
$$P(C^4H^5)^3(C^{10}H^{11}).I.$$

The second of these compounds forms crystals of great beauty. Triphosphamylamine also furnished the compounds—

$$P(C^{10}H^{11})^3(C^2H^3).I,$$
$$P(C^{10}H^{11})^3(C^4H^5).I,$$
$$P(C^{10}H^{11})^4.I.$$

These iodides are readily decomposed by oxide of silver; in this way are obtained iodide of silver and some very soluble compounds, endowed with considerable alkaline power, and capable of completely neutralizing the strongest acids. These oxides readily neutralize muriatic acid, and furnish crystallizable compounds, which form fine combinations with bichloride of platinum.

The analysis of the chloroplatinates of tetraphosphomethylammonium and tetraphosphæthylammonium led to the formulæ—

$$P(C^2H^3)^4.Cl, PtCl^2, \text{ and } P(C^4H^5)^4.Cl, PtCl^2.$$

By double decomposition with the silver-salts (nitrate, sulphate, &c.); the preceding iodides give iodide of silver and salts of the phosphammoniated bases.

By substituting terchloride of arsenic, $AsCl^3$, for the terchloride of phosphorus, the authors have obtained equally good results; chloride of bismuth appears to act in a similar manner.—*Comptes Rendus*, Nov. 12, 1855, p. 831.

Researches on Pyroxyline. *By* A. Béchamp.

In a paper dated October 4, 1852[*], the author showed that by the action of gaseous ammonia upon a solution of pyroxyline in æther and alcohol, this substance is decomposed, giving rise to nitrate of ammonia, and a compound less nitrated than pyroxyline, the formula of which he stated to be—

$$C^{24}H^{17}O^{17},4NO^5.$$

In a subsequent note (July 25, 1853)[†] he announced the regeneration of the cotton of the pyroxyline by the action of protochloride of iron.

When nitric acid acts upon an organic substance under favourable conditions, it combines with it, with elimination of water. But in the action of the alkalies and reducing agents upon these compounds, some, such as nitrobenzine, are converted into new azotized products containing all the nitrogen of the nitrated compound; whilst others, such as nitric æther, reproduce the original material, and the nitric acid is eliminated either in its natural state or in the form of different azotized compounds. Pyroxyline behaves like nitric æther and the nitrates in general.

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[*] Chem. Gaz. vol. x. p. 427. [†] *Ib.* vol. xii. p. 11.

Caustic potash and ammonia, in contact with water and pyroxyline, abstract the nitric acid, forming compounds less nitrated than pyroxyline, but this action is ill-defined. It is singular that the action of caustic potash upon pyroxyline produces sugar, which must be regarded as formed under the influence of an alkali; for it did not exist in the pyroxyline, which only reproduces cotton under the influence of reducing agents.

The action of the alkalies upon the solution of pyroxyline in æther and alcohol is very well defined. Caustic potash and ammonia abstract nitric acid, and a compound is formed of the formula

$$C^{24}H^{17}O^{17},3NO^5.$$

The author adds two new experiments to prove that pyroxyline is of the nature of a nitrate:—

1. When pyroxyline is treated with sulphuric acid with 2 equivs. of water, it is not dissolved, and the temperature does not rise, but the odour of free nitric acid is soon perceived; and if at the end of twenty-four hours the liquid be diluted with water, filtered, and distilled, nitric acid passes without reddish vapours. Pyroxyline therefore contains nitric acid.

2. If, instead of reducing the pyroxyline by protochloride of iron, it is reduced by the acetate of the same base, no deutoxide of nitrogen is evolved as with the protochloride, but ammonia is formed, as may be easily proved by treating the filtered liquid with caustic potash. This is the case also with the nitrates, for when these are treated with iron filings and acetic acid, their acid is converted into ammonia. This may perhaps furnish a new method of determining nitric acid.

By this treatment all the nitrogen of the pyroxyline is converted into ammonia; but when nitrobenzine is treated with protacetate of iron, it remains in the molecule of the new compound (*aniline*) which is produced. Thus there appear to be two groups of nitric derivatives which are far from being homogeneous, and which are characterized by the regeneration of the original compound in one case, and the formation of a nitrated compound in the other.

The possibility of returning from the nitric derivative to the original type is therefore the bond of union between nitric æther, nitric glycerine, nitric mannite, starch, quenite, cellulose, &c. All these relations are analogous, not to the nitrated compounds of the nature of nitrobenzine, but to the æthers, acetic æther for example, and the compounds of glycerine with acids. In conformity with these views, the author proposes the following formulæ for these compounds:—

$C^{24}H^{17}O^{17},5NO^5,2HO$ = pentanitric cellulose.
$C^{24}H^{16}O^{16},4NO^5,HO$ = tetranitric cellulose.
$C^{24}H^{17}O^{17},3NO^5$ = trinitric cellulose.
$C^{20}H^{20}O^{20}$ = cellulose.

Comptes Rendus, Nov. 12, 1855, p. 817.

On Hordeic Acid, a new Member of the Series of Fatty Acids.
By F. Beckmann.

When 4 lbs. of dry barley are distilled with 6 lbs. of sulphuric acid previously diluted with 4 lbs. of water, a distillate is obtained, upon which float small laminæ which are fatty to the touch; similar laminæ are also condensed in the colder portion of the neck of the retort.

This body appears in irregular laminæ of crystalline structure; it is not altered by exposure to the air, is completely insoluble in water, readily soluble in alcohol, and still more readily in æther. The alcoholic solution has a distinctly acid reaction. When heated upon paper, it makes a greasy spot; at 140° F. it melts to a clear oily fluid, which again solidifies at 131° F. When fused on platinum foil, it burns with a brightly luminous flame and without residue. It combines with alkalies, and the solution froths like soap and water. It expels carbonic acid from the alkaline carbonates. When a large quantity of water is added to the solution of the soap, chloride of sodium separates white flakes from it. Acids separate the body unchanged from the lye. Analysis gave—

C	71·31	24 =	144	72
H	12·68	24	24	12
O	..	4	32	16

The silver-salt contained 34·79 per cent. of silver; calculated, 35·18. Æther extracts from barley a fat, coloured green by chlorophyll; this, when decolorized by charcoal, is obtained as a brown oil. This oil dries in the air, and has a peculiar odour like that which prevails in a malt-kiln. The fat may be easily saponified with alkalies, and by the addition of muriatic acid to the soap a mixture of two fatty acids is obtained, of which one is solid and crystalline, melting at 133°·7 F., and solidifying at 118°·4 F., whilst the other is fluid. These properties of the two fatty acids obtained from the fat of barley appear to prove that they are different from hordeic acid. It was also ascertained that they did not furnish hordeic acid by distillation with sulphuric acid. Lastly, it is worthy of notice, that the barley, when exhausted of its fat by æther, furnished hordeic acid by distillation with dilute sulphuric acid. It is probable that hordeic acid might be obtained from the unsaponified fat of the barley.—*Journ. für Prakt. Chem.*, lxvi. p. 52.

On the Crystallization of Platinum from Fusion.
By J. W. Mallet, Ph.D.

Having recently prepared some bichloride of platinum as a reagent by dissolving scraps of platinum foil, wire, &c. in nitromuriatic acid, I poured off the yet strongly acid solution before the whole of the metal had disappeared, and washed and dried the remaining scraps. Among them there were five or six small beads of platinum, which had been melted off from the end of a wire (of about one-fortieth of an inch in diameter) by the oxyhydrogen blowpipe-flame. I was surprised to observe that these globules, which were spherical, and quite smooth and brilliant before the acid had acted upon them, afterwards presented distinct traces of crystallization, resembling to the eye the little polyhedral beads of phosphate of lead which are obtained by fusing that salt before the blowpipe.

Some of the minute faces were plane or nearly so, but most of them were slightly rounded, like those of many crystals of diamond. They presented for the most part the peculiar lustre of a metal with very minute striæ on the surface, but some of the facets were brilliant.

The prevailing form seemed to be the tetrakis-hexahedron, of which there was one very distinct example; and beside this, faces of the octahedron, and *perhaps* of the cube with truncated angles—combinations of the cube with the octahedron—were recognizable on other beads.

Some of the globules were apparently *groups* of minute crystals, while one or two seemed to be distinct individuals.

The weight of the largest was not more than 0·11 grm.

The crystalline faces were no doubt rendered visible by the *dissecting* action of the acid, in the same way that the structure of a lump of alum may, as is well known, be brought out by partial solution in water, the chemically homogeneous mass offering at different points a greater or less resistance to the solvent, dependent upon the positions of these points with reference to the crystalline axes, just as the actual hardness of resistance offered to mechanical abrasion differs at different parts of the surface of a crystal.

The assumption of distinct crystalline structure by platinum under the circumstances mentioned, is remarkable from the extremely high melting-point of the metal, the small quantity fused in each bead, and therefore the very short time in which each must have passed from the liquid to the solid state.—Silliman's *Journal*, November 1855.

On Pipitzahoic Acid. By M. C. Weld.

This acid, which was investigated in Liebig's laboratory by the author, was discovered by Dr. Rio de la Loza in Mexico; it is prepared from a root which the aborigines call *Raiz del Pipitzahuac*, and use as a purgative. The acid analysed by Weld crystallizes from alcohol in tufts of laminar crystals; from the ætherial solution it crystallizes in small, shining, obliquely-rhombic tables, the angle of the base 84° and 96°, the inclination of the base to the surface of the prism 94°. They have a distinct cleavage in the direction of the greater diameter. The acid is of a golden colour, and nearly insoluble in water; it is thrown down by water from its alcoholic and ætherial solutions in the form of voluminous flocculent masses. It fuses at 212° F., forming a red fluid, which solidifies in a crystalline form, and is volatilized at a temperature above 212° F.

Its composition is $C^{30} H^{20} O^{6}$. Caustic alkalies and alkaline earths give a deep purple precipitate with its solutions. Its alkaline salts dissolve readily in water, alcohol, and æther. The copper salt is insoluble in water, and can be precipitated by water from its alcoholic solution; it forms a thick greenish-brown mass, but does not crystallize. It is soluble in æther, and its composition is $C^{30}H^{19}CuO^{6}$.—Liebig's *Annalen*, xcv. p. 191.

Note on the Oxidizing Properties of Perchlorinated Æther.

By F. MALAGUTI.

When a mixture of equivalent quantities of an alkaline formiate and perchlorinated æther is distilled, it furnishes protochloride of carbon ($C^{4}Cl^{4}$), carbonic acid, water, and an alkaline chloride.

In this reaction the alkaline metal evidently combines with a portion of the chlorine of the æther, and the oxygen of the æther unites with that of the salt, in order to complete the combustion of the other elements; the perchlorinated æther having lost 1 molecule of chlorine and all its oxygen, must pass to the state of *protochloride of carbon.* Thus,—

$$\underset{\substack{\text{Perchlorinated}\\\text{æther.}}}{C^{4}Cl^{5}O} + \underset{\substack{\text{Alkaline}\\\text{formiate.}}}{C^{2}HMO^{4}} = \underset{\substack{\text{Carbonic}\\\text{acid.}}}{C^{2}O^{4}} + HO + \underset{\substack{\text{Protochloride}\\\text{of carbon.}}}{C^{4}Cl^{4}} + \underset{\substack{\text{Alkaline}\\\text{chloride.}}}{MCl}$$

The oxidizing property of perchlorinated æther is therefore evident, as a portion of the elements of this body assists in the complete combustion of the elements of the salt. But as this might be an exceptional case, owing to the fact that all the elements of the formiate were in contact with a sufficient quantity of the oxidizing principles, the author proceeded to ascertain whether perchlorinated æther performs the same part in other instances.

He made a fresh experiment with fused acetate of soda, and obtained protochloride of carbon, crystallizable acetic acid, chloride of sodium with no trace of carbonate, and a gaseous mixture composed of carbonic acid, oxide of carbon and hydrogen:—

$$2C^{4}Cl^{5}O + 2C^{4}H^{3}NaO^{4} = C^{4}H^{4}O^{4} + 2C^{4}Cl^{4} + 2NaCl + \begin{cases} 2CO^{2} \\ 2CO \\ 2H \end{cases}$$

In this case the formation of crystallizable acetic acid could not have been foreseen. The appearance of this acid led him to suppose that perchlorinated æther only acts upon the salts of volatile acids, and that all the organic alkaline salts of this description would behave like the acetates. Experiment has confirmed this view; he failed with the citrates, tartrates, &c., but succeeded perfectly with the butyrates, valerates, benzoates, succinates, pyrocitrates, phthalates, camphorates, and salicylates. All these salts, when distilled with perchlorinated æther, furnished protochloride of carbon, normal acid, alkaline chlorides without carbonate, and a gaseous mixture of carbonic acid and combustible gases. The salts with biatomic acids generally furnish the anhydride and water, instead of the normal acid. Thus, when an alkaline camphorate is distilled with perchlorinated æther, the ordinary products are obtained, but in place of normal camphoric acid, water and fine crystals of anhydrous camphoric acid are formed; as the anhydride + water represents the normal acid, the reactions of the biatomic salts are the same as those of the monoatomic salts. The only exception is presented by the alkaline salicylates, which instead of salicylic acid form various substances, soluble in the alkalies, which have not been examined by the author.

The author has also succeeded in similar experiments with acetate of baryta, lime, and lead; but the readiness with which acetate of copper is decomposed by heat, prevents the action of the perchlorinated æther. In fact, each body furnishes the products peculiar to its destructive distillation.

From these facts the author concludes that perchlorinated æther will be found exceedingly serviceable in the laboratory, as by means of it several highly interesting products may be easily obtained, the preparation of which by ordinary processes is tedious, difficult and expensive. Thus with perchlorinated æther, which is easily prepared, we may immediately obtain,—

Protochloride of carbon	$C^4\,Cl^4$
Sesquichloride of carbon	$C^4\,Cl^6$
Chloroxethose	$C^4\,Cl^3\,O$
Chlorinated aldehyde	$C^4\,Cl^4\,O^2$.

By isolating chloroxethose with bromine, we have perchlorobrominated æther $= C^4\,Cl^3\,O\,Br^2$.

By passing water into the product of the rapid distillation of perchlorinated æther, we get a solution of very pure chloracetic acid $= C^4\,Cl^3\,HO^4$.

If alcohol be substituted for the water, chloracetic æther $= C^4\,H^5\,O, C^4\,Cl^3\,O$, is produced.

And if ammonia be substituted for the water or alcohol, chloracetamide $= C^4\,Cl^3\,H^2\,NO^2$, is obtained.—*Comptes Rendus*, Oct. 22, 1855, p. 625.

On Insolinic Acid, a Product of the Oxidation of Cuminic Acid.

By A. W. Hofmann.

Whilst endeavouring to purify cuminic acid by ebullition with chromic acid, I observed that the former underwent a progressive alteration by the action of this reagent. By treatment for twenty-four hours, cuminic acid is completely converted into an acid which is insoluble in alcohol and æther, and nearly insoluble in water; for this reason I have given it the name of *insolinic acid*. When purified by the ordinary methods, this body gave on analysis the following proportions,—$C^9\,H^4\,O^4$. But the analysis of the salts showed that this formula must be doubled, *insolinic acid* being a bibasic acid.

I have examined a series of salts, of which the following is the composition :—

Free insolinic acid........	$C^{18} H^8 O^8$
Silver-salt	$C^{18} (H^6 Ag^2) O^8$
Copper-salt..............	$C^{18} (H^6 Cu^2) O^8 + HO, CuO$
Barium-salt..............	$C^{18} (H^6 Ba^2) O^8$
Calcium-salt (at 212° F.) ..	$C^{18} (H^6 Ca^2) O^8 + 6HO$
Calcium-salt (at 266° F.) ..	$C^{18} (H^6 Ca^2) O^8$.

Potassium-Salts.

Neutral salt	$C^{18} (H^6 K^2) O^8$
Acid salt................	$C^{18} (H^7 K) O^8$
Salt of potassium and sodium	$C^{18} (H^6 KNa) O^8$.

If this acid be regarded as an isolated body, it possesses but little interest for the chemist; but, on the other hand, it acquires a certain degree of importance when considered with regard to the relations which it presents with other compounds. It is already some years since M. Gerhardt pointed out that there existed a series of bibasic acids containing 8 atoms of oxygen, which presented mutual relations perfectly analogous to those observed between the bodies which compose the curious series of monobasic acids with 4 atoms of oxygen, of which the first term is formic acid, and which are generally known as the series of fatty acids. These series of acids have the closest connexion amongst themselves, and very conclusive experiments have shown that we may readily pass from one to the other; such is the instance of the conversion of butyric into succinic acid, effected by M. Dessaignes under the influence of oxidizing agents. The following table will show clearly what we have just remarked :—

Formic acid	$C^2 H^2 O^4$		
Acetic acid	$C^4 H^4 O^4$	Oxalic acid	$C^4 H^2 O^8$
Propionic acid ..	$C^6 H^6 O^4$	?	$C^6 H^4 O^8$
Butyric acid	$C^8 H^8 O^4$	Succinic acid ..	$C^8 H^6 O^8$
Valeric acid	$C^{10} H^{10} O^4$	Pyrotartaric acid	$C^{10} H^8 O^8$
Caproic acid	$C^{12} H^{12} O^4$	Adipic acid	$C^{12} H^{10} O^8$
Œnanthylic acid	$C^{14} H^{14} O^4$	Pimelic acid....	$C^{14} H^{12} O^8$
Caprylic acid....	$C^{16} H^{16} O^4$	Suberic acid....	$C^{16} H^{14} O^8$
Pelargonic acid..	$C^{18} H^{18} O^4$	?	$C^{18} H^{16} O^8$
Rutic acid......	$C^{20} H^{20} O^4$	Sebacic acid ..	$C^{20} H^{18} O^8$

The existence and the mode of formation of insolinic acid shows that there exists a series of bibasic acids with 8 atoms of oxygen, which present the same relation as that observed between succinic and butyric acid, to the series of monobasic acids with 4 atoms of oxygen, of which the first term is benzoic acid, and which is generally known as the series of aromatic acids. At present we only know a few terms of this series of bibasic acids, but the list of the aromatic acids is still very incomplete. In the following table I have brought together the numbers belonging to these two groups of bodies:—

Benzoic acid....	$C^{14}H^{6}O^{4}$	?	$C^{14}H^{4}O^{8}$
Toluylic acid ..	$C^{16}H^{8}O^{4}$	Phthalic acid .. Terephthalicacid	$C^{16}H^{6}O^{8}$
?	$C^{18}H^{10}O^{4}$	Insolinic acid ..	$C^{18}H^{8}O^{8}$
Cuminic acid ..	$C^{20}H^{12}O^{4}$	?	$C^{20}H^{10}O^{8}$

If we adopt the carbon as the starting-point for the comparison, it is evident that insolinic acid corresponds with the acid placed between toluylic and cuminic acid, which is still unknown. Besides insolinic acid, there are at present only the phthalic acid of M. Laurent and the terephthalic acid of M. Caillot, which belong to the group of bibasic acids, these two isomeric acids corresponding with toluylic acid. Benzoic acid and cuminic acid are not yet represented in the series of bibasic aromatic acids.

To prepare the acid corresponding with benzoic acid, I treated cymene, which when oxidized by dilute nitric acid furnishes toluylic acid, with chromic acid; but the cymene only furnished insolinic acid.

During my stay in Paris, M. Persoz called my attention to some experiments which he made ten years ago upon the oxidation of oil of cumin. It appears that the existence of insolinic acid was anticipated by that chemist, but his observations are not accompanied by analytical data.—*Comptes Rendus*, Oct. 29, 1855, p. 718.

On the Behaviour of Solution of Perchloride of Mercury towards Bases. By H. ROSE.

By means of carbonate of baryta, and other substances with a weak basic action, but especially by means of solutions of chloride of ammonium, the various oxides can only be brought into two divisions, with respect to their stronger or weaker basic properties; but with a solution of perchloride of mercury three such sections may be established. This method has the advantage that we may know immediately, from the colour of the precipitate, to which of the three divisions the base tested by perchloride of mercury belongs.

The first division includes the strong bases, which, when added in excess to a solution of perchloride of mercury, produce a yellow precipitate of pure peroxide of mercury, even at ordinary temperatures.

These are the hydrates of the alkalies, potash, soda and lithia, and of the three alkaline earths, baryta, strontia and lime, as well as the solutions of the alkaline silicates; not only the common *Liquor silicum*, but also the solution of the crystallized silicate of soda, the only soluble silicate which has yet been artificially obtained.

To the second section belong the weaker bases, or strong bases the strongly basic properties of which are somewhat obscured by combination with a weak acid. With the solution of perchloride of mercury they give a precipitate of a reddish-brown colour, which consists of a compound of perchloride of mercury, in which the chloride cannot be converted into oxide at the ordinary temperature, even by an excess of the base. An exactly similar compound is also formed in solution of perchloride of mercury by the strongest bases, when these are added only in small quantities; but an excess of these quickly converts the chloride into oxide, and the colour of the precipitate changes immediately from reddish-brown to yellow.

We may consequently also test the strength of many weak acids by means of the solution of perchloride of mercury, their combination with strong bases removing these to a different section from that to which they originally belonged.

To this category belong the neutral alkaline carbonates, the sesquicarbonate of soda, the alkaline borates (both the neutral and biborates), the borates of the alkaline earths, magnesia, hydrate of magnesia, the compounds of carbonate of magnesia with hydrate of magnesia, the artificially prepared neutral carbonate of magnesia ($MgO\,CO^2+3HO$), and oxide and carbonate of silver. It is however difficult to determine whether oxide of silver belongs to the first or second division. To a certain extent also some alkaline phosphates and pyrophosphates belong to this section.

The third section includes the great number of bases which do not decompose solution of perchloride of mercury. The alkaline bicarbonates and the carbonates of the alkaline earths also belong to it.

From this it follows that in the humid way carbonic acid must be a stronger acid than boracic acid, as even the biborates of the alkaline earths do not decompose the solution of perchloride of mercury. But both the carbonic and boracic acids are stronger acids in the humid way than silicic acid, which, when in combination with the alkalies, is not capable of obscuring their basic properties any more than water, as appears from the behaviour of these compounds with the solution of perchloride of mercury.

This section also includes magnesite, the native neutral carbonate of magnesia, whilst the artificially prepared neutral carbonate of magnesia belongs to the second division.—*Berichte der Akad. der Wiss. zu Berlin*, 1855, p. 579.

On the Combustion of Organic Bodies by means of the Chromates of Lead and Potash. By Dr. MAYER.

Liebig has already recommended the employment of a mixture of the chromates of lead and potash in the combustion of organic bodies, and by his advice Richardson effected the combustion of coal in this manner in 1837. This method has since been neglected, but Dr. Mayer has recently made new experiments upon it in the combustion of very different substances, with the most satisfactory results.—Liebig's *Annalen*, xcv. p. 204.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Compounds of Stibæthyle. By W. Merck.

The author has made some experiments to ascertain the constitution of iodide of stibæthyle. He first studied the action of ammonia on this body; but it soon became evident that the correct formula of the body could be ascertained in this manner.

The author therefore tested further the behaviour of stibæthyle towards iodide of stibæthyle. An ætherial solution of stibæthyle was prepared in a retort filled with carbonic acid; it was divided into two parts, of which one was exactly saturated with iodine and added to the other. That in this case the action of the stibæthyle upon iodide of stibæthyle does not take place instantaneously appears from the fact, that when this solution is rapidly evaporated a continual fuming is observed, and an oily fluids remains, which still contains much free stibæthyle; this was also observed in the action of ammonia upon iodide of stibæthyle. The ætherial solution was therefore left to spontaneous evaporation in a current of dry carbonic acid, which was effected in the following manner.

The solution placed in a beaker was covered with a large funnel with a wide tube, through the aperture of which a current of dry carbonic acid was passed through an india-rubber tube, which reached to the surface of the fluid; the evaporation thus takes place in the current of dry carbonic acid. After about half of the æther had evaporated, remarkably regular, strongly lustrous octohedra of considerable size and hardness were obtained, which even in external appearance agreed exactly with those which were prepared by the action of ammonia upon iodide of stibæthyle. By further evaporation more crystals of the same form were obtained, but finally a salt crystallized, which was essentially distinguished from the crystals first deposited both by its greater solubility in water and its different form.

1. The octohedral crystals gave on analysis,—

Sb	37·68	1	=	129	37·61
C	20·70	12		72	20·99
H	4·52	15		15	4·37
I	37·10	1		127	37·03

2. The smaller crystals last obtained gave 36·52, 36·84, 36·80 per cent. of iodine. These analyses therefore agree with the formulæ—

1. $(SbAe^3)I$, 2. $(SbAe^3H)I$.

From this it follows that the formula of iodide of stibæthyle cannot be $SbAe^3 I^2$. There remains therefore only a doubt between the formulæ $(SbAe^3) I, HI$ and $(SbAe^3 H) I^2$, as proved by the following experiments.

1. If an alcoholic solution of iodine be added to a solution of $(SbAe^3) I$ in anhydrous alcohol, the iodine is but slowly taken up, but if it be gently heated, the colour of the iodine disappears very quickly; the same thing also takes place when a little water is added. If iodine be added as long as its colour disappears, a white powder separates, and from the solution filtered therefrom crystals of iodide of stibæthyle are obtained by spontaneous evaporation. If, on the other hand, the aqueous solution of these octohedral crystals of $(SbAe^3) I$ be mixed with hydriodic acid, the so-called iodide of stibæthyle is instantaneously thrown down; this dissolves completely in alcohol, and may be obtained in beautiful crystals from the solution.

But if iodine be added to the crystals last obtained, it cannot be brought to disappear, and hydriodic acid produces no separation of iodide of stibæthyle from this solution.

2. If the oxide corresponding with the octohedral iodide $(SbAe^3) I$ be prepared by means of oxide of silver, and dilute muriatic acid be added to its aqueous solution, each drop of the acid produces a white turbidity, which disappears again immediately on stirring. If the addition of the muriatic acid be continued, a moment occurs in which the turbidity becomes permanent, and if more muriatic acid be added, a perfectly colourless fluid, insoluble in water, separates; this possesses all the properties of chloride of stibæthyle. It contains 25·16 per cent. of chlorine.

If this chloride of stibæthyle be put into an aqueous solution of the oxide, it dissolves immediately, and after the evaporation of the solution a salt of the formula $(SbAe^3) Cl$, readily soluble in water, is obtained; and if this solution be again mixed with muriatic acid, the chloride of stibæthyle is again precipitated.

3. If iodide of stibæthyle be prepared directly, that is to say, by saturating an alcoholic solution of stibæthyle with iodine, and the ætherial solution of this compound be treated with an alcoholic solution of the oxide of $(SbAe^3) I$, it furnishes by spontaneous evaporation the same octohedral crystals which are obtained by the action of stibæthyle upon iodide of stibæthyle.

Oxide of Stibtriæthyle, $(SbAe^3) O$.—This body is obtained by the complete decomposition of the aqueous solution of iodide of stibtriæthyle by pure freshly-precipitated oxide of silver, and separating the aqueous solution of the oxide from the iodide of silver by filtration. A considerable quantity of oxide of silver is dissolved in the fluid, and is only partially separated by evaporation on the water-bath; it must therefore be got rid of by careful precipitation with hydriodic acid; muriatic acid cannot be employed for this purpose, as oxide of stibtriæthyle dissolves chloride of silver in considerable quantity. The solution is then evaporated, first on the water-bath, and finally *in vacuo* over sulphuric acid; in this way the oxide is obtained in the form of a thick, syrupous, limpid mass, which is readily soluble in water and alcohol, but dissolves in smaller quantity in æther.

Between the fingers it feels slippery, like concentrated potash lye; it has an intensely bitter and biting taste, and a strongly alkaline reaction, and is in general a strong base. It is rather volatile, and if a glass rod moistened with muriatic acid be held over the vessel in which the solution of the oxide is evaporating on the water-bath, slight white clouds are observed; but even after long standing *in vacuo* over sulphuric acid there is no perceptible loss. On mixing it with water, a considerable evolution of heat takes place.

Oxide of stibtriæthyle precipitates the oxides from solutions of the persalts of copper, mercury, and lead; they do not dissolve in an excess of the precipitant. The oxide also behaves in the same way with the salts of protoxide of manganese and iron and of peroxide of iron. In salts of oxide of zinc and alumina the base produces white precipitates, which however dissolve again in an excess of the precipitant.

Sulphate of Stibtriæthyle, $(SbAe^3)O+SO^3$, was obtained in the form of a transparent gum-like mass which may be triturated into a white powder. It deliquesces vary readily in the air, and dissolves in any quantity of water.

The *nitrate,* $(SbAe^3)O+NO^5$, is very soluble in water; it solidifies into a radiate mass.

Carbonate of Stibtriæthyle, $(SbAe^3)O, CO^2$, is obtained by the decomposition of the iodide with carbonate of silver. After evaporation on the water-bath, the compound remained in the form of a thick syrupous mass, without traces of crystallization.

Acetate of Stibtriæthyle.—If a solution of oxide of stibtriæthyle be saturated with acetic acid, and the solution be evaporated on the water-bath, there remains a thick syrupous residue, which even by long standing in a warm place could not be brought to crystallize.

Iodide of Stibtriæthyle.—This is obtained either directly by the exact saturation of the oxide with hydriodic acid, by adding a dilute solution of the latter until a permanent turbidity is produced, which is then made to disappear by a drop of the oxide; or by the methods above described, by the action of ammonia or stibæthyle upon hydriodate of iodide of stibtriæthyle, $(Sb\,Ae^3)I, HI$.

This compound is the most interesting, on account of its great tendency to crystallize; the most beautiful crystals are obtained by the spontaneous evaporation of the ætherial solution. These are perfectly transparent, limpid, hard, glassy, inodorous, and nearly unalterable in the air. After lying in the air for weeks no trace of decomposition is perceptible; they are perfectly anhydrous, and lose nothing in weight by long standing *in vacuo* over sulphuric acid. The crystals are either octohedra or tetrahedra, and their form is the same both from aqueous and alcoholic solutions.

If an aqueous solution of iodide of stibtriæthyle be added to an aqueous solution of bromide of mercury, a yellow precipitate is first of all produced, which however very quickly passes to red; the decomposition is then complete. No doubt in the first moments of the precipitation the yellow modification of iodide of mercury is produced, which is afterwards converted into the red one. In this respect iodide of stibtriæthyle differs essentially from iodide of stibæthylium, which, as is well known, forms a compound of 3 atoms of iodide of mercury with 1 atom of iodide of stibæthylium, which separates in the form of an oily fluid when gently heated.

If alcoholic solutions of equal atomic weights of bromide of mercury and iodide of stibtriæthyle be employed, no precipitate is produced, and if the fluid be evaporated a slightly yellowish oil remains, which separates in proportion as the alcohol evaporates; if this oil be shaken with water, no iodide of mercury separates immediately, and the solution contains bromide of stibtriæthyle.

Bromide of Stibtriæthyle, $(SbAe^3)Br$, scarcely appears to crystallize. Chloride of stibtriæthyle is extremely soluble.

With sulphur, stibtriæthyle forms a compound, which no doubt agrees with the formula $(SbAe^3)S, HS$. If the alcoholic solution of oxide of stibtriæthyle be saturated with sulphuretted hydrogen and left to evaporate spontaneously, beautiful crystals are obtained, agreeing in their properties with sulphuret of stibæthyle.—*Journ. für Prakt. Chem.*, lxvi. p. 56.

On the Action of the Metallic Chlorides upon Iodide of Lead.

By A. Engelhardt.

According to the author's experiments, iodine is separated from the metallic iodides only by perchloride of iron and perchloride of copper; the other metallic chlorides, M^2Cl^3 and MCl^2, and the protochlorides, separate no iodine. The author has studied this behaviour with iodide of lead, and found that the latter chlorides furnish the following compounds with iodide of lead:—

$$PbI + MCl = PbCl + MI,$$
$$3PbI + M^2Cl^3 = (PbCl)^3 + M^3I^3,$$
$$2PbI + MCl^2 = (PbCl)^2 + MI^2.$$

If the iodide of lead be present in excess, chloride of lead is not formed, but compounds are produced which may be regarded as iodide of lead in which a portion of the iodine is replaced by chlorine.

Action of the Chlorides MCl *upon Iodide of Lead.*—Iodide of lead was mixed with a great excess of chloride of lead and boiled. After long boiling, the iodide of lead loses its orange-yellow colour, and becomes converted into a pale yellow powder; but the supernatant fluid on cooling deposits only white, shining, acicular crystals of chloride of lead. The yellow powder was again extracted with water, and the aqueous solution on cooling furnished yellow, shining, acicular crystals (A). The residue, again treated with boiling water, gave a solution from which yellow crystals (B) similar to A were deposited. When the residue was further treated with boiling water, the solution furnished at last only six-sided laminæ of iodide of lead.

The acicular crystals A and B have a beautiful sulphur-yellow colour, but the crystals B were distinctly yellower than A; under the lens they appeared as thin, transparent, yellow prisms. In their external appearance these crystals present a great resemblance to the PbCl crystallized from water, but they differ in their colour. They contain lead, chlorine, and iodine; the amount of lead in A was 68·93 per cent., and in B 59·35 per cent.

Similar needles are obtained by mixing a hot saturated solution of iodide of lead with a solution of chloride of lead. To obtain these yellow needles of the same nature, chloride of lead must always be present in excess, and in such quantity that all the iodide of lead is converted into a yellow powder; but the solution must also be saturated with chloride of lead. When iodide of lead is mixed with an excess of chloride of lead, boiled with water, and the solution filtered, crystals are formed on cooling; if these be taken out and the fluid again employed in the treatment of the residue, nearly all the iodide of lead may be converted into these yellow needles. The needles which are obtained after each cooling of the solution are exactly similar in external appearance, and also resemble the crystals A and B. The shining sulphur-yellow crystals C and D, obtained in this manner, contained C 63·96, and D 63·23 per cent. of lead. The solution from which the yellow acicular crystals separated, furnished crystals of chloride of lead on evaporation.

When iodide of lead is employed in excess instead of chloride of lead, the solution from which the yellow acicular crystals are to separate must be very slowly cooled, because otherwise crystals of iodide of lead are also deposited. When this takes place, the solution must be again heated with the separated yellow needles and the laminæ of PbI, and a little evaporated; only yellow acicular crystals are deposited afterwards.

These yellow needles, which are produced by the action of chloride of lead upon iodide of lead, consist of such proportions that their formula places them between $PbI^{\frac{1}{2}} Cl^{\frac{1}{2}}$ and PbCl.

Of the group of chlorides MCl, the author tested the following, —NaCl, BaCl, CaCl, MnCl, CoCl ,NiCl, ZnCl, SnCl, AgCl, and also that of HgCl.

When chloride of silver is boiled with iodide of lead and water, iodide of silver and chloride of lead are obtained when AgCl is employed in excess; when PbI is in excess, yellow needles, similar to those above described, are produced.

By the action of other chlorides of the above group MCl, the following results were produced:—

The iodide of lead, when boiled with a strong solution of MCl, is converted into a pale yellow powder, and partially dissolved; the filtered solution deposits yellow needles on cooling. If the solution be filtered in a cold vessel, orange-yellow tablets of PbI are first deposited; but as soon as the vessel is warmed these tablets again dissolve, and on subsequent cooling only yellow needles are deposited. To obtain these needles perfectly pure, the author heated the filtered fluid until everything which had separated and sunk to the bottom had again dissolved; it was then allowed to cool gradually, but the fluid must be poured away from the needles before it has become quite cold, as otherwise tablets of PbI are frequently deposited. The needles obtained must also be washed with a dilute solution of the same metallic chloride by the action of which they have been obtained, because they are decomposed by pure water.

The needles obtained by the action of the above-mentioned metallic chlorides form shining thin prisms, the colour of which is far yellower than that of the above compounds, A, B, C, D. In the light they decompose very readily, acquiring a black colour and separating iodine. This decomposition takes place on that surface of the needles which is turned towards the light, and it is effected more rapidly by the direct action of the solar rays than in ordinary light. They are decomposed by water both in the cold and also when boiled; they acquire an orange-yellow colour, and iodide of lead is separated.

When the yellow powder, or the yellow needles obtained by the action of the metallic chloride upon iodide of lead, are boiled with water, they are decomposed; an orange-coloured powder is produced, and a solution is obtained, which on cooling deposits tablets of PbI. If these be removed and the solution evaporated, yellow needles are obtained, which resemble those above marked A; if these be treated with not too great a quantity of nitric acid, iodine is separated, and chloride and nitrate of lead remain. Such yellow needles obtained by the action of NaCl upon PbI contained 54·12 per cent. Pb; needles (F) obtained by the action of BaCl upon PbI contained 55·89 Pb; and the action of MnCl upon PbI furnished crystals (G) containing 50·8 per cent. The needles G are decomposed by light much more rapidly than the needles E and F; a quantity decomposed by light, with perceptible separation of iodine, furnished on analysis 51·11 per cent. of lead.

The compounds obtained in this manner have the formula $PbI^x Cl^y$; but the quantity of iodine is larger than that of the chlorine, so that $x > \frac{1}{2}$ and $y < \frac{1}{2}$; the formula $PbI^x Cl^y$ consequently stands between the formulæ PbI, which contains 44·93 per cent. of lead, and $PbI^{\frac{1}{2}} Cl^{\frac{1}{2}}$, which requires 56·05 per cent. Pb. The amount of lead in E and F approaches pretty closely to this latter formula, but that in G is nearer the formula $PbI^{\frac{2}{3}} Cl^{\frac{1}{3}}$, which contains 51·78 per cent. Pb.

Action of the Chlorides $M^2 Cl^3$ *upon Iodide of Lead.*—The author tested the action of the chlorides $Fe^2 Cl^3$, $Al^2 Cl^3$, and $Cr^2 Cl^3$ upon iodide of lead.

A solution of $Fe^2 Cl^3$ acts upon PbI as upon KI. When boiled, iodine separates, and chloride of lead and protochloride of iron are obtained, $PbI + Fe^2 Cl^3 = I + PbCl + (FeCl)^2$. When PbI is present in excess, instead of PbCl, yellow needles, $PbI^x Cl^y$ ($x < \frac{1}{2}$ and $y > \frac{1}{2}$), similar to those marked C, are obtained.

Perchloride of aluminium and perchloride of chromium (obtained by dissolving the hydrated peroxide in muriatic acid) act upon PbI in the same way as the chlorides MCl, that is to say, a yellow residue is obtained, and the solutions furnish yellow needles on cooling. The yellow needles obtained by the action of perchloride of aluminium contain 50 per cent. Pb, and are therefore similar to the needles G; needles decomposed by light contained 52·30 per cent. Pb. The yellow needles obtained are decomposed very readily by boiling with water, and iodine is separated. The solution from which the yellow needles had been deposited, when evaporated to the consistence of a syrup, furnished crystals of perchloride of aluminium containing water. The mother-liquor of these crystals had a brown colour and contained much iodine, which it deposited on treatment with perchloride of iron.

Action of the Chlorides MCl^2 *upon Iodide of Lead.*—Of the group MCl^2 the author investigated the action of $SnCl^2$, $PtCl^2$, $HgCl^2$, and $CuCl^2$ upon PbI. Perchloride of copper acts upon PbI in the same way as upon KI. On boiling, iodine is separated, and chloride of lead and protiodide of copper are obtained, $PbI^2+CuCl^2 = CuI+(PbCl)^2+I$.

$SnCl^2$ acts upon PbI in the same way as the chlorides MCl; $HgCl^2$ in action upon PbI furnishes HgI^2 and PbCl.

$PtCl^2$, when boiled with an excess of PbI, gives a black precipitate and a colourless solution; the solution on cooling deposits yellow needles of $PbI^x Cl^y$, like those marked A. The black precipitate, when boiled with water, gives PbI to the latter; and after continued treatment with water, it appears under the lens as a uniform black powder, which apparently is a compound of PbI with PtI^2, for when heated with Fe^2Cl^3, iodine is separated, and it furnishes a black precipitate of PtI^2 and white needles of chloride of lead.—*Bull. de St. Pétersb. Classe Phys. Math.*, xiv. p. 145.

On the Saponification of Neutral Fatty Bodies by Soaps.

By M. J. Pelouze.

One of the oldest manufacturers of mould-candles communicated to the Jury of Universal Exposition a very important modification of the process of saponification of fatty bodies, and of tallow in particular, by means of lime. He has ascertained that the proportion of lime necessary for this saponification, which he had long reduced from 15 to 8 or 9 per cent. of the weight of the fatty matter, might be further diminished by half, and reduced to only 4 per cent. merely by exposing the mixture of lime, water, and fatty matter to a high temperature. The operation is performed upon several thousand kilogrammes of tallow at once in a metallic caldron, which is kept for several hours at a temperature corresponding to a pressure of 5 or 6 atmospheres. The œconomy of an operation which allows us to diminish by half the quantity of sulphuric acid required for the decomposition of the calcareous soap is very intelligible.

It appeared to me interesting to study attentively a saponification effected in the presence of a quantity of base so small that it does not amount to a twenty-fourth part of the acidified fatty matter. I prepared a calcareous soap by double decomposition, by pourin a solution of chloride of calcium into an aqueous solution of commercial soap. The precipitate, when well washed, was placed in a small Papin's digester with about its weight of water and 40 per cent. of olive-oil. The vessel was kept for about three hours in an oil-bath at a temperature between 311° and 329° F. The supernatant water in the digester was evaporated; it left a syrupous residue presenting all the properties of glycerine.

The precipitate, boiled with water acidulated with muriatic acid, furnished a completely acidified fatty matter, for it was directly and entirely soluble in alcohol and the alkalies. In a word, the reaction presented all the characters of the ordinary decomposition of the neutral fatty bodies by free alkalies. Except that the hardness of the new calcareous soap was less, it might have been regarded as a saponification by caustic lime.

Another experiment was made directly upon Marseilles soap, mixed with its weight of water and a quarter of its weight of olive-oil. The temperature and the operation were the same. The substance after the reaction had all the properties of an acid soap; it was soluble in cold alcohol, or in an aqueous solution of potash or soda. Acids separated a fatty substance, which was also entirely soluble in cold alcohol and alkaline solutions.

From the two preceding experiments, it results that the soaps, like the alkalies themselves, are capable of causing the splitting of fatty bodies into glycerine and fatty acids; from this it will be understood how I am justified in giving this note the apparently paradoxical title of "Saponification of Neutral Fatty Bodies by Soaps."

I have also ascertained that at a temperature of 329° F. water does not act upon oils. To split them, it is necessary that the mixture of fatty matter and water should attain and retain for a very long time the temperature of 428° F., assigned by M. Berthelot for this latter saponification.

In England, where the firm of Price and Co. produces immense quantities of stearic candles, the saponification is effected by the action of the vapour of water at a still higher temperature. It produces fatty acids and nearly pure free glycerine, which is of great service in the arts and in medicine.

In the new reactions just mentioned, we can understand that water at a temperature of 302° to 320° F. may decompose a neutral soap into an acid soap and a very basic soap, and that the latter acts secondarily upon the new quantity of fatty matter, in the same way as a free alkali. M. Chevreul's observations on the action of water on the soaps agree with this explanation. M. de Milly's experiment, which served as the starting-point of my paper, is explained in a similar manner.

We may suppose that the saponification of tallow by means of only 4 per cent. of its weight of lime, presents several distinct phases in which a basic or neutral soap is first formed, and afterwards changes into a comparatively acid soap.

The observations of which I have just given a summary find a very simple interpretation in the works of M. Chevreul on the fatty bodies. They give reason to expect new kinds of decomposition in this numerous and important class of substances. From the moment when the elements of water alone act in resolving the neutral fatty bodies into acids and glycerine, we may expect to see science and the arts multiply and vary the phænomena of saponification.

Some months since I made known some reactions of this nature, perhaps even more curious still than those just referred to, namely, the spontaneous saponification of all fatty bodies without exception, with or without the contact of the air, by the simple mechanical division of the seeds in which they are contained.—*Comptes Rendus*, Dec. 3, 1855, p. 973.

On Pyroterebic Acid. *By* J. CHAUTARD.

A relation exists between angelicic acid and a series of other acids which may be expressed by the general formula $C^{n} H^{n-2} O^{4}$. These acids are decomposed by alkalies into hydrogen and equal equivalents of acetic acid and of a second acid of the series $C^{n} H^{n} O^{4}$. Thus, for example,—

$C^{6} H^{4} O^{4}$, acrylic acid $+ 2KO, HO = C^{4} H^{3} KO^{4} + C^{2} HKO^{4} + 2H$.
$C^{10} H^{8} O^{4}$, angelicic acid $+ 2KO, HO = C^{4} H^{3} KO^{4} + C^{6} H^{5} KO^{4} + 2H$.
$C^{36} H^{34} O^{4}$, oleic acid $+ 2KO, HO = C^{4} H^{3} KO^{4} + C^{32} H^{31} KO^{4} + 2H$.

It appears that some other acids range themselves with these, such as Städeler's damaluric acid, $C^{14} H^{12} O^{4}$, the acid discovered by Heintz in mutton-fat, $C^{36} H^{34} O^{4}$, and Rabourdin's pyroterebic acid, $C^{12} H^{10} O^{4}$.

The author has tested the behaviour of the latter acid towards potash, and found that it is in fact homologous with acrylic, angelicic, and oleic acids. Pyroterebic acid is produced by exposing to heat the terebic acid obtained by Bromeis by treating oil of turpentine with nitric acid. It is an oleaginous colourless fluid, heavier than water; it boils at 410° F. In this respect it differs from butyric acid, with which it might be confounded from its odour and taste. The author has analysed it with the following results:—

		Amount of silver in the salt. Found.	Calculated.
C	63·15		
H	8·78	49·25	49·54

If this acid be let fall in drops upon fusing potash, hydrogen is abundantly evolved, and the residue contains equal equivalents of acetic and butyric acids.—*Journ. de Pharm. et de Chim.*, 3 ser. xxviii. p. 192.

Analysis of Veratrine. *By* G. MERCK.

The author has analysed perfectly crystallized veratrine, the colourless crystals of which soon effloresce in the air, becoming porcellaneous and very friable. These crystals are insoluble in water, but become turbid and lose their form. When concentrated sulphuric acid is poured over them, they first become yellow, and then of a beautiful red. With concentrated muriatic acid, especially when heated, they furnish a dark violet solution. It completely neutralizes dilute acids. From his analyses of veratrine, and of the gold and platinum double salts, the author derives the following formulæ:—

Veratrine .... $=C^{64}H^{52}N^{2}O^{16}$.
Perchloride of gold and veratrine.. $=C^{64}H^{52}N^{2}O^{16}, HCl+AuCl^{3}$.
Sulphate..................... $=C^{64}H^{52}N^{2}O^{16}, HO\,SO^{3}$.

Liebig's *Annalen*, xcv. p. 201.

ANALYTICAL CHEMISTRY.

On the Acidimetry of Acetic Acid.

By E. Chambers Nicholson *and* David S. Price, Ph.D.*

The general method for estimating the amount of free acid in a liquid by means of a standard solution of an alkali or alkaline carbonate, is known not to afford correct results when applied to the determination of acetic acid. The failure of this process, which has been ascribed to two causes, first, to the difficulty of ascertaining by the aid of the vegetable colouring matters the precise point of saturation of the acid, and secondly, to the volatility of the acid, we find to be owing to the alkalinity of the acetate produced, the neutral acetates of potash and soda, as well as those of the earths, exhibiting very marked alkaline reactions to test-paper. From this it will therefore be evident that the saturating point, as ascertained by the above volumetrical process, will represent that at which the alkaline action of the acetate predominates over that of the remaining free acid, and will therefore not give the absolute quantity of acid present.

This is rendered apparent by a comparison of the results obtained by testing acetic acid of different degrees of concentration by different methods, as in the following experiments:—

	Per-centage of hydrate of acetic acid found by			
Acetic acid.	standard solution of carb. soda.	carbonate of lime.	carbonate of baryta.	Fresenius and Will's method.
1. Glacial.........	87·9	99·6	99·4	99·3
2. Dilute	45·3	52·8	52·3	52·0
3. More dilute than in experiment 2..	22·1	25·5	25·7	25·3

In the above experiments about 100 grs. of acid were taken for each determination.

The standard solution employed contained 12·5 grs. of carbonate of soda in 100 grain-measures of water, and was added to the acid, which was diluted with from 30 to 40 vols. of water until an alkaline reaction was obtained by test-paper, the fluid being warmed towards the end of the operation to expel carbonic acid.

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* Communicated by the Authors.

The determinations by means of the carbonates of baryta and lime were conducted as follows.

A weighed amount of the pure precipitated carbonate was added to the acid diluted with from 15 to 20 parts of water, and allowed to digest, at first in the cold, and afterwards heated to expel all carbonic acid; the portion remaining undissolved was collected on a filter, dried, and weighed, and the amount thus found subtracted from the original quantity taken.

The determination by the method of Fresenius and Will was made with pure bicarbonate of potash.

The results obtained by the three last methods we believe to indicate the real per-centage of acetic acid.

The opinion expressed by Williams*, that a solution of acetate of potash to which alkali has been added will evolve acetic acid on evaporation, and that on this account fused acetate of potash possesses an alkaline reaction, we have not found to be correct.

We find that if carbonate of potash be added to acetic acid until an alkaline reaction is manifested, the product will on evaporation evolve acetic acid; that this is owing, not to a decomposition of the acetate, but simply to the elimination of that portion of acid that had not been neutralized, owing to its presence having been masked by the alkalinity of the acetate formed, is proved by fusing the residue obtained by evaporation, then dissolving it in water, and resubmitting it to distillation, when the distillate will be found to be neutral. In order to establish further proofs of the correctness of this view, we have made the following experiments. 2 fluid ounces of acetic acid (containing 80 per cent. real acid), diluted with water, were neutralized with the theoretical quantity of carbonate of potash, the solution distilled to dryness in a retort, and finally completely fused. The distillate thus obtained was perfectly neutral to test-paper, and was found to be only pure water. The fused mass remaining in the retort, when dissolved in water, gave a solution that reacted powerfully alkaline, but was nevertheless free from either hydrate or carbonate of potash, affording no precipitates with baryta-water, or an ammoniacal solution of chloride of calcium, either before or after it had been boiled with carbonate of ammonia, which was added for the purpose of converting any free alkali into carbonate. A similar result was obtained with acetate of soda, which in order to ensure purity had been four times recrystallized. The solution of this salt was found to be very alkaline to test-paper.

These experiments prove that the neutral acetates of potash and soda, if carefully fused, do not suffer decomposition; also that the strength of acetic acid cannot be correctly estimated by a standard solution of either an alkali or an alkaline carbonate, on account of the alkalinity of the acetate produced, for the same reason that this process is inapplicable for the estimation of free phosphoric acid, the neutral alkaline salts of which are also alkaline to test-paper.

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* Pharm. Journ., vol. xiii. p. 594.

NOTE.—The test-paper employed in the above experiments was that known as Griffin's neutral test-paper.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

New Mode of Preparation of Aluminium, and of some simple Metallic and Non-metallic Bodies. By M. H. SAINTE-CLAIRE DEVILLE.

NEARLY two years ago I undertook a series of experiments to determine the precise equivalent of aluminium, by operating upon small quantities of metal in a state of absolute purity; subsequently, in order to check my first numbers, I have had to try different methods of procuring pretty large masses of unexceptionable material. For a long time I failed, in consequence of the nature of the vessels usually employed; but this first difficulty has been overcome by means which I shall shortly communicate to the Academy. A second obstacle is caused by the foreign matters which always accompany aluminous compounds; fortunately, within the last few months, considerable masses have been found of a mineral which has hitherto been very rare, the *kryolite* of Greenland, a double fluoride of aluminium and sodium, which appears to be nearly pure. I am indebted to the kindness of MM. Hofmann and H. Rose for several kilogrammes of this substance, upon which I have made several experiments.

It appears that in England a certain quantity of aluminium has been procured from kryolite by means of the pile; but the experiments of H. Rose first showed the possibility of extracting the metal from this mineral, and for this purpose he employed sodium. To effect this reduction, it is sufficient to put into a porcelain crucible alternate layers of sodium and pulverized kryolite mixed with a little common salt. The porcelain crucible is placed in an earthen one, and heated to a bright red heat until complete fusion. The material is stirred with a rod of earthenware, and allowed to cool. All the aluminium is collected in a lump, which is found at the bottom of the cold mass. Whilst the matter is liquid, and even when it is partially solidified at the surface, a combustible gas is evolved, which bursts through the thick crust, and takes fire in the air. It is no doubt a phosphorous vapour, as indicated by its odour; and, moreover, the presence of phosphoric acid in kryolite may be detected by molybdate of ammonia. This is the process that I have employed; it differs but little from that of Prof. H. Rose. In operating with a porcelain crucible, the aluminium contains silicium; with an iron crucible, it contains iron, as stated by M. Rose, who however has thus obtained aluminium of great ductility.

This experiment has suggested others. I had frequently, and long since, attempted to reduce the double chloride of aluminium and sodium by means of sodium; although the reaction was completely effected, I did not obtain the lump of metal, and M. Rammelsberg has arrived at the same result. It is sufficient, however, to add a little fluoride of calcium to the mixture, to cause all the aluminium to collect in lumps at the bottom of the crucible. This experiment, which MM. Debray and Paul Morin have been so good as to try for me in my absence in the laboratory of the Ecole Normale, has always succeeded very well with them, and they have prepared several hundred grammes of tolerably pure aluminium in this manner. It will be seen from what follows, that the alkaline fluorides, dissolving alumina, must be regarded as the best flux of aluminium. It is thus that we must explain this experiment, which appears to me to furnish an advantageous process for the manufacture of this metal.

The composition of kryolite is represented by the formula—

$$Al^2 Fl^3, 3(NaFl), \text{ or rather } Al^{\frac{2}{3}} Fl, NaFl;$$

if this latter formula be compared with that of the acid fluate of soda (hydrofluate of fluoride of sodium), HFl, NaFl, it will be seen that it is only necessary to replace H in this latter salt by $Al^{\frac{2}{3}}$ to obtain kryolite. If therefore we take acid fluate of soda and calcined alumina in the proportions indicated by these formulæ, mix them intimately together, and heat them gradually in a platinum crucible, only very small quantities of hydrofluoric acid escape; and at a moderate temperature a very fluid and limpid matter is obtained, the weight of which corresponds very nearly with that of kryolite calculated by the preceding formulæ. When treated with sodium, the new matter furnishes aluminium, which proves that it is formed with fluoride of aluminium, and not with alumina. Analysis will show whether it is the same fluoride as the natural fluoride of aluminium and sodium.

The same result is obtained by mixing alumina and fluoride of sodium moistened with concentrated hydrofluoric acid. The mass becomes hot; it is then dried and fused, and aluminium may be extracted from it. The same experiment also succeeds with fluoride of potassium; and if this be in excess in the mixture, the matter may be treated with water after fusion, by which the fluoride of potassium is dissolved, leaving a crystalline, very fusible substance, which no doubt is kryolite with a potash base, or some analogous body, for from this mixture aluminium may also be extracted.

In all my experiments I have found it difficult to remove silica sufficiently to prevent my aluminium from containing silicium, often in pretty considerable quantities. Besides, the returns from kryolite, as remarked by M. H. Rose, and especially from this kind of artificial kryolite, are always very small.

In the course of these experiments I have often been able to prove the very peculiar property of the alkaline fluorides, which renders them an almost universal solvent at a high temperature. It may be easily shown, by taking a very fusible mixture of the fluorides of potassium and sodium; at a red heat a large quantity of silica and titanic acid may be dissolved in it, besides a little alumina and a great many other substances, and it is singular that this addition of foreign substances causes fusibility, and communicates to the bath a fluidity comparable to that of water.

I have thought that such a substance, which may be readily traversed by electric currents, would be an excellent excipient for matters which under ordinary circumstances resist the action of the pile. Thus by dissolving silica in the double alkaline fluoride and passing the current through it, silicium is produced, which, if a platinum electrode be employed, combines with that metal. At the positive pole numerous bubbles of a gas, which can only be oxygen, are disengaged. It is not fluorine, for if a certain quantity of common salt be added to the bath, no chlorine is perceived, and it is well known that the chlorides are decomposed before the fluorides. The same experiment gave analogous results with titanic acid.

But with alumina it is quite different; the double alkaline fluoride dissolves but little of it, and under the influence of the electric current sodium is burnt at the negative pole and fluorine disengaged at the positive pole; it is recognized by the very strong odour of hydrofluoric acid, which is produced in the flame of the lamp over which the experiment is made; this effect is very well explained by the beautiful experiments of M. Fremy on the electrolysis of the fluorides. All this proves,—1, that alumina resists the action of the pile better than the alkaline fluorides; 2, that alumina is not reducible by sodium, which might have been expected; 3, that the contrary is the case with silica.

Silica, in fact, is reduced by sodium, and I have succeeded in preparing silicium with great ease by bringing vapour of sodium into contact with silica, or even with very pure pounded glass. This silicium is identical with that prepared from chloride of silicium.

The only difficulty which occurs in the experiments just described results from the nature of the vessels which must be employed and the alterability of the electrodes; for coke is very quickly disintegrated in the fluoride baths, when they are employed for instance in the preparation of silicium.—*Comptes Rendus*, Dec. 10, 1855, p. 1053.

On a new Gold Varnish which does not lose its Colour by exposure to Air and Light.

A very beautiful and permanent gold varnish may be prepared in the following manner:—2 ozs. of the best French garancine are digested in a glass vessel with 6 ozs. of alcohol of spec. grav. 0·833, for twelve hours, pressed, and filtered. A solution of clear orange-coloured shell-lac in similar alcohol is also prepared, filtered, and evaporated until the lac has the consistence of a clear syrup; it is then coloured with the tincture of garancine. Objects coated with this have a colour which only differs from that of gold by a slight brownish tinge. The colour may be more closely assimilated to that of gold by the addition of a little tincture of saffron.—*Archiv der Pharm.*, cxxxiv. p. 78.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Dec. 6, 1855. (Sir Benjamin Brodie, Bart., V.P., in the Chair.)

"Results of the Examination of certain Vegetable Products from India."—Part I. By John Stenhouse, LL.D., F.R.S.

Through the kindness of my esteemed friend Dr. Royle, I have been permitted to select such vegetable products from the extensive collection at the India House as seemed most likely to repay the trouble of investigation. My attention, during the last twelve months, has been chiefly directed to three of these vegetable substances; and the results of their examination I now take the liberty of submitting to the Royal Society, to be followed by those of the others as they may be completed.

Datisca cannabina.

The first of these substances which I examined consisted of a quantity of the roots of the *Datisca cannabina*, from Lahore, where this plant is employed to dye silk of a fast yellow colour. The roots, which had been cut into pieces about 6 or 8 inches long, were from a half to three-quarters of an inch in thickness. They had a deep yellow colour. A decoction of the leaves of the *Datisca cannabina* was examined by Braconnot in 1816, who discovered in it a crystallizable principle, to which he gave the name of *datiscine*. Braconnot, of course, did not subject this substance to analysis, but he described its appearance and properties in an exceedingly accurate manner*. The observations of Braconnot had fallen into such entire oblivion, however, that for many years past, we find in most of the larger systems of chemistry the term datiscine used as synonymous with inuline. Thus in Brande's 'Chemistry,' vol. ii. p. 1168, we find it stated that a variety of names had been given to inuline, such as "dahline, datiscine," &c.

The bruised roots were extracted in a Mohr's apparatus by long-continued digestion with wood-spirit. The liquor obtained, which had a dark brown colour, was concentrated by distilling off a portion of the wood-spirit. The brown syrupy liquid remaining in the retort, on being poured into open vessels and standing for some time, deposited a resinous matter containing merely traces of a crystalline substance. When this syrupy liquid, however, was treated with about half its bulk of hot water, the greater portion of the brown resin was rapidly deposited, and the mother-liquor having been poured off and left to spontaneous evaporation, deposited a considerable quantity of an imperfectly crystallizable substance resembling grape-sugar. These crystals are datiscine containing a considerable amount of resinous matter. The datiscine, however, is rendered perfectly pure by treatment with a solution of gelatine, to remove any trace of tannic acid, and repeated crystallizations out of weak spirits of wine.

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* Annales de Chimie et de Physique, 1816, iii. 277.

Properties of Datiscine.—Datiscine, when pure, is perfectly colourless. It is very soluble in alcohol, even in the cold, boiling alcohol dissolving any amount of it. By slow spontaneous evaporation, its alcoholic solutions yield small silky needles arranged in groups. Cold water does not dissolve much of it, but it is tolerably soluble in boiling water, the hot solutions on cooling depositing it in shining scales.

Datiscine is not very soluble in ether; but an ethereal solution, when evaporated, yielded larger crystals than were obtained by any other method. On adding water to an alcoholic solution of datiscine, no precipitate is immediately obtained, unless the solution is greatly concentrated; but on standing, very pure, pale yellow-coloured crystals of datiscine separate.

When datiscine is heated to about 180° C., it melts, and if the heat be increased, it burns, evolving an odour of caramel, and leaves a voluminous charcoal. If datiscine be heated in a close vessel while a stream of dry air is slowly passed over it, a small quantity of a crystalline substance sublimes. Datiscine and its solutions have a very bitter taste; and though it does not produce any change on test-paper, I think there is reason to regard it as a feebly acid body.

It dissolves in solutions of the fixed alkalies and ammonia, also in lime- and baryta-water. The addition of an acid to these solutions causes the precipitation of the datiscine.

The aqueous solution of datiscine is precipitated by neutral and basic acetates of lead, and chloride of tin. These precipitates have a bright yellow colour. Salts of copper produce greenish, and those of peroxide of iron brownish-green precipitates. In consequence of the lead salts forming such gelatinous precipitates, they could not be employed for determining the equivalent of datiscine.

Action of dilute Sulphuric Acid on Datiscine.—When an aqueous solution of datiscine is boiled for a few minutes with very dilute sulphuric acid, it deposits a crystalline substance. On examining the solution filtered from the crystals, very distinct evidences of the presence of sugar were obtained. These experiments show therefore that datiscine, like salicine and similar bodies, belongs to the class of glucosides, and is a copulated compound of sugar and another substance which I shall call "datiscetine."

Datiscetine.—Datiscetine in its general appearance and properties closely resembles datiscine, but on a closer examination these two substances are found to differ essentially both in composition and properties. Datiscetine when pure assumes the form of fine needles which are nearly colourless. It is easily soluble in alcohol, a hot alcoholic solution, on cooling, depositing the greater portion in crystalline groups. It is almost insoluble in water, consequently datiscetine is precipitated from its alcoholic solutions by the addition of water. It dissolves in ether in almost any quantity, and is deposited on the evaporation of that liquid in needles. These properties of datiscetine enable us to obtain it in a tolerably pure state, even when very impure datiscine is employed in its preparation.

Properties of Datiscetine.—Datiscetine has no taste. When heated it melts like datiscine, but the heat required is much higher than for that body. It recrystallizes on cooling. By operating very cautiously, a portion of the datiscetine may be sublimed. The sublimate, however, appears to be altered datiscetine. Datiscetine when burned does not emit the odour of caramel. Datiscetine, like datiscine, dissolves in alkaline solutions, and is reprecipitated by the addition of an acid. An alcoholic solution of acetate of lead added to an alcoholic solution of datiscetine produces a deep yellow precipitate, which can be easily washed both by alcohol and water. This precipitate therefore was subjected to analysis, and from the results obtained, the formula $C_{30}H_8O_{10}+2PbO$ was calculated, which agrees with the formula ($C_{30}H_{10}O_{12}$) derived from the analysis of datiscetine.

Analysis of Datiscine.—It is difficult to calculate a formula for datiscine, the numbers of which shall agree with those found by analysis. When, however, the decomposition of datiscine into datiscetine and sugar is taken into consideration, it seems probable that the formula for datiscine is

$$\begin{array}{ccc}\text{Datiscetine} + & \text{sugar} & = \text{datiscine} \\ C_{30}H_{10}O_{12} + & C_{12}H_{12}O_{12} & = C_{42}H_{22}O_{24}.\end{array}$$

If the formula $C_{42}H_{22}O_{24}$ be correct, the decomposition of datiscine by dilute sulphuric acid would be analogous to that of salicine when treated in the same way.

Dilute hydrochloric acid, like dilute sulphuric acid, decomposes datiscine, converting it into datiscetine and sugar. On boiling an aqueous solution of pure datiscine for some hours, traces of sugar could be detected, thus showing that a small portion of the datiscine had been decomposed.

It has been already shown that datiscine dissolves in cold solutions of potash without decomposition. When boiled, however, with a strong solution of potash for some time, decomposition takes place, and the precipitate, thrown down by the addition of an acid, has all the properties of datiscetine. In this respect, therefore, datiscine agrees with tannin and similar glucosides, which yield the same products when acted upon by acids and alkalies. Yeast and emulsine appeared to exert no action on solutions of datiscine.

Action of Nitric Acid on Datiscine and Datiscetine.—Cold nitric acid of the ordinary strength acts violently upon datiscetine, brown vapours are disengaged, and a resinous substance is produced, which is ultimately dissolved, forming a dark red liquid, which, when evaporated, yields crystals of nitropicric acid.

Datiscine treated in the same way yields nitropicric and oxalic acids.

When datiscine is boiled with dilute nitric acid it dissolves, and the solution obtained, when cooled, deposits pale yellow crystals, which agree in every way with the properties ascribed to nitrosalicylic acid.

On allowing datiscine to stand in contact with dilute nitric acid in the cold it gradually dissolves, the solution, when left to evaporate *in vacuo*, depositing a mixture of oxalic and nitropicric acids.

Action of Potash on Datiscine and Datiscetine.—It was stated in a previous part of this paper that datiscine and datiscetine dissolve in cold solutions of the alkalies without decomposition, and that datiscine, when boiled with potash, is decomposed with the formation of datiscetine. It only remained, therefore, to try the action of fused hydrate of potash. Datiscetine, when added in small successive portions to fused hydrate of potash, assumed a deep orange colour, and then dissolved with the evolution of hydrogen gas. When the disengagement of hydrogen had ceased, the mass was dissolved in water and supersaturated with hydrochloric acid. A partly resinous substance separated, which, by sublimation, yielded perfectly colourless, long crystals closely resembling benzoic acid. Their solution in water on the addition of perchloride of iron gave that deep violet tint which disappears on the addition of hydrochloric acid, and is so characteristic of salicylic acid.

Action of Chromic Acid on Datiscetine.—On distilling datiscetine with bichromate of potash and sulphuric acid a liquid came over, containing no oily drops, but having the smell of salicylous acid, and which, when tested with a persalt of iron, formed a purple-coloured solution characteristic of that acid.

It follows therefore, I think, from the experiments already detailed, that datiscine, like salicine, phloridzine, &c., is a glucoside, and that it approaches nearer to salicine than any other glucoside, with the exception of populine, yet known.

I will conclude this account of datiscine by proposing the following practical application. As is well known, the colouring matter of madder, when boiled with dilute sulphuric acid, is changed into sugar and garancine, a new dye-stuff, which, for many purposes, is found superior to that originally present in the madder. Within the last twelve months Mr. Lieshing, by treating the colouring matters in weld and quercitron bark with dilute sulphuric acid, has resolved them into new colouring matters, which are but slightly soluble in water, and are found nearly three times more powerful as dye-stuffs than the original colouring matters from which they had been produced.

As datiscine, when boiled with dilute sulphuric acid, undergoes a perfectly similar transformation, being resolved into sugar and datiscetine, which has a much higher colouring power than the datiscine which has produced it, I have not the least doubt that silk dyers, who may hereafter employ solutions of *Datisca cannabina*, will find it highly advantageous to convert their datiscine into datiscetine by boiling it with dilute sulphuric acid.

Oil of the Ptychotis Ajowan.

The *Ptychotis Ajowan* is an umbelliferous plant well known in India for its aromatic and carminative properties. When its seeds are distilled with water they readily yield between five and six per cent. of an essential oil resembling in smell that of oil of thyme. When this oil is left in shallow vessels to spontaneous evaporation at low temperatures, it deposits a large quantity of beautiful crystals, which are identical with the stearopten brought from India by the late Dr. Stocks, and described by me in a short notice in the December Number of the 'Pharmaceutical Journal' for 1854.

The crude oil was rectified, and the portion which came over between 160° C. and 164° C. was collected separately and carefully rectified over sodium. Its boiling-point was found to be 172° C., and its composition isomeric with oil of turpentine, namely

$$C_{10}\,H_8 \text{ or } C_{20}\,H_{16}.$$

The stearopten obtained from the less volatile portion of the oil was purified, and formed large flat rhombohedral crystals, which have been carefully measured by Professor Miller of Cambridge. When subjected to analysis it gave the formula

$$C_{20}\,H_{14}\,O_2 \text{ or } C_{20}\,H_{13}\,O_1\,HO.$$

In the notice of the stearopten of this oil which appeared in the 'Pharmaceutical Journal,' from the examination of the small quantity then at my disposal, a different formula was deduced, which I now withdraw, and substitute the preceding formula, $C_{20}\,H_{14}\,O_2$, in its stead.

When the crystalline stearopten is digested for eight or nine days with the strongest nitric acid, it is gradually converted into a crystallizable acid, apparently containing no nitrogen. This acid is but slightly soluble even in boiling water, but is deposited in needles on the cooling of the solution. It is very soluble in alcohol and ether, from which it is deposited in crystals. Both its silver and its baryta salts are crystallizable, and appear very stable. It seems to me to be a new acid, and this I hope soon to be able to ascertain.

When the stearopten is gently warmed with oil of vitriol it dissolves, and, on cooling, solidifies into a crystalline mass. This new compound, which is a copulated acid, dissolves readily in hot water, and, on cooling, is deposited in large scaly crystals, of a mother-of-pearl lustre. It forms both a crystallizable lead and baryta salt.

When the stearopten is distilled with a mixture of peroxide of manganese and sulphuric acid, it yields a substance exceedingly analogous in almost every respect to the thymöil obtained by Lallemande by subjecting the stearopten of oil of thyme to similar treatment. As the details of Lallemande's experiments have not yet been published, it would be premature to pronounce with absolute confidence on the identity of the stearoptens from the *Ptychotis* and oil of thyme; but if not identical, as I rather apprehend they are, they are certainly extremely similar bodies*.

Gum of the Gardenia lucida, *Roxb.* *(the Decamalee Gum of Scinde)*.

The specimen of this gum on which I operated was evidently very old. It formed a hard, dry mass, of a dark brown colour, with numerous patches of a greenish-yellow matter disseminated through it. It had but a faint odour, unless freshly fractured or gently heated, when it smelt like the urine of the cat.

A comparatively recent specimen of this gum, which I saw in the hands of the late Dr. Stocks, had merely the consistence of candied honey, and an exceedingly offensive odour. Dr. Stocks informed me that the fresh gum was employed as a dressing for wounds, as it kept off the flies. The resin was digested in strong spirit of wine, till a saturated solution was obtained. This, on cooling, immediately deposited some yellow amorphous flocks. These were separated by filtration, and the clear liquid slowly evaporated *in vacuo*. On standing a few days, it deposited a quantity of golden yellow slender crystals, about half an inch in length. The crystals had considerable lustre, and were very brittle. To this crystalline substance I purpose giving the provisional name of *gardenine*. Gardenine is nearly insoluble both in cold and hot water. It dissolves pretty readily in alcohol, but much less readily in ether; ether yielding bright yellow solutions, out of which it crystallizes on cooling. Alkalies, such as ammonia, do not appear to increase its solubility. It is more soluble in hot hydrochloric and sulphuric acids than in water, and is precipitated, apparently unchanged, on the addition of water. Its alcoholic solutions give no precipitate with ammonio-nitrate of silver, or with basic acetate of lead. When gardenine is digested with concentrated nitric acid, it is rapidly decomposed; nitropicric acid, but apparently no oxalic acid, being produced.

Unfortunately, from the very small quantity of resin at my disposal, I was unable to prepare a sufficient amount of the gardenine either to subject it to analysis or to examine it more particularly. Dr. Royle has, however, commissioned a large quantity of the resin from India, which I trust will ere long enable me to complete its examination. Gardenine appears to belong to the tolerably numerous class of indifferent crystallizable resins, of which it is certainly one of the most beautiful.

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* Since this paper was communicated to the Royal Society, a notice of the Ptychotis oil, by Dr. Haines, of the Bombay College, was read before the last meeting of the Chemical Society. Dr. Haines has generally arrived at similar conclusions to my own. He regards, however, the carbohydrogen portion of the oil not as isomeric with oil of turpentine, but as $C_{20} H_{14}$.

His formula for the stearopten is the same as that given in this paper; and he regards it as identical with Lallemande's thymole.

Dr. Haines, however, appears not to have observed the crystalline acid produced by the action of nitric acid on the stearopten.

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No. CCCXIX.—February 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Relations between certain Bodies differing by H^2 *and* O^2.

By T. STERRY-HUNT*.

THE study of organic chemistry has shown the existence of very remarkable relations between certain compounds whose formulæ differ by nC^2H^2, forming thus series the members of which are in arithmetical progression. These relations of homology, far from being limited to the compounds of carbon, are but examples of that harmony of numbers which Laurent saw, which Dumas has recognized in the equivalents of the elements, and which will become for the science of chemistry a principle as wide in its application as those of atomic weights and volumes. The formulæ of neutral, basic, and hydrated salts, which differ by nM^2O^2, and by nH^2O^2, offer a perfect analogy with the homologous series of Gerhardt; and there exist also relations which deserve to be signalized between bodies differing by the proportions of oxygen and hydrogen.

The volatile alkaloids present a striking example of the latter case. The bases of Wurtz are represented by $(C^2H^2)n+NH^3$; but there exists another series whose formula is $(C^2H^2)n+NH$. Piperidine, $C^{12}H^{13}N$, belongs to this last series; and by its volatility, its causticity, and even by its odour is related to the ammonias of Wurtz, from which it differs by containing 2 atoms less of hydrogen. Although these ammonias do not readily part with these 2 atoms of hydrogen, the corresponding compounds, in which antimony replaces nitrogen $(C^2H^2)n+SbH^3$, lose directly H^2 by the action of chlorine and nitric acid, and yield bases having the formula $(C^2H^2)n+SbH$.

The chloride of kakodyle, as Gerhardt has shown, is to be regarded as the chlorhydrate of an alkaloïd, *arsine*, C^4H^5As, which is an arsenical base belonging to the same series as piperidine and stibæthine. These bases are evidently to the ammonias what the aldehydes are to the alcohols.

The alkaloïds harmine and harmaline, and the two series of fatty acids $(C^2H^2)n+O^4$ and $(C^2H^2)n+H^2O^4$, represented by the acetic and acrylic acids, are also examples which enter into the same class as the preceding, and lead us to admit an intimate relation between bodies differing by H^2.

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* Communicated by the Author.

Chemistry also presents examples of bodies which are related by their chemical and physical properties, and differ by the number of equivalents of oxygen. Benzoic aldehyde with its derivatives may be taken as the type of one series of homologous bodies, while salicylic aldehyde represents another series of compounds differing from the last by O^2, but offering with them a constant correspondence in their characters. The alkaloids quinine and cinchonine, and the malic and tartaric acids, are also examples of related bodies whose formulæ differ by O^2. Crystallography comes to the support of these resemblances, for Nicklès, and after him Pasteur, has observed that the bimalate and bitartrate of ammonia are isomorphous. The chlorate of potash, $ClKO^6$, is also, according to Nicklès, hemimorphous with the perchlorate of the same base, $ClKO^8$*.

The sulphites and the carbonates present, according to Muspratt, a perfect correspondence in their composition and their crystalline forms, the formulæ of the two series being $S^2 M^2 O^6$ and $C^2 M^2 O^6$. The sulphates, which differ by O^2 from the common formula of the sulphites and carbonates, offer some remarkable relations of form with the latter. Hausmann has shown that the carbonates, such as arragonite, witherite, and cerusite, may be regarded as isomorphous with the corresponding sulphates, and Dana has pointed out the following relations:—The *dreelite* of Dufrénoy, which is a double sulphate of lime and baryta, crystallizes in rhombohedra isomorphous with the sulphato-carbonate *susannite*, $3PbO, CO^2 + PbO, SO^3$. This last compound, which is dimorphous, occurs also in prisms (*leadhillite*) isomorphous with sulphate of lead, while another sulphato-carbonate, *lanarkite*, $PbO, CO^2 + PbO, SO^3$, is isomorphous with the double sulphate of lime and soda, *glauberite*. It would therefore appear that the carbonates and sulphates, being isomorphous, crystallize together in variable proportions, although they differ from one another, as the malates from the tartrates, and the chlorates from the perchlorates by O^2.

If from these resemblances we admit that sulphur, oxygen, and carbon may in some sort replace each other, we can readily explain the reaction between the ferrocyanides and the deutoxide of nitrogen. The nitroprussides of Playfair are to be regarded as polycyanides which have exchanged an equivalent of cyanogen, $C^2 N$, for one of deutoxide of nitrogen, $O^2 N$. This view of the functions of oxygen and carbon finds many applications in the history of the derivatives of cyanogen. (*Comptes Rendus*, Dec. 24, 1855, p. 1167.)

The ferrocyanides being $Cy^6 Fe^2 M^4$, the ferricyanides are represented by $Cy^6 Fe^2 M^3$; but the iron being regarded as existing in these salts in the form of *ferricum*, $Fe^{\frac{2}{3}} = fe$, their formula becomes $Cy^6 fe^3 M^3$. I have in another place described the nitroprussides as bibasic, but Dr. Playfair found that even the silver-salt contains a portion of hydrogen, its formula being $Cy^5 Fe^2 Ag^2, NO, HO = Cy^5 fe^3 Ag^2 H, NO^2$, or a ferricyanide in which NO^2 replaces an equivalent of cyanogen, NC^2. This derivation of the nitroprussides is sustained by the observation of Dr. Playfair, that the first step in the process with the yellow prussiate is the production of a ferricyanide, which afterwards absorbs nitric oxide, and liberates gaseous cyanogen, the reaction being simply one of replacement. The formulæ of these three polycyanides are then as follows:—

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* Nicklès has also observed that in several hydrated salts of organic acids, a variation in the quantity of the water does not change the angles of the prism, but produces a difference in the modifications of the pyramids, thus offering cases of hemimorphism.

Ferrocyanides	$C^{12}\ Fe^2\ M^4\ N^6$
Ferricyanides..............	$C^{12}\ fe^3\ M^3\ N^6$
Nitroprussides	$\left\{\begin{matrix}C^{10}\\ O^2\end{matrix}\right\} fe^3 \left\{\begin{matrix}M^2\\ H\end{matrix}\right\} N^6.$

On the Solubility of Silica. *By* H. LUDWIG.

Professor Ludwig of Jena has made experiments upon the solubility of silica in water, aqueous acids, alkalies, and salts, from which he concludes that silica behaves like the oxides of antimony towards alkalies and acids. As the oxides of antimony obstinately retain acids and bases, so also does silica. The experiments are as follows:—

1. Finely triturated carnelian from Jena was evaporated with solution of potash in a platinum cup. The mass was moistened with water in a porcelain dish, acidulated with muriatic acid, and evaporated to dusty dryness; the residue was heated with muriatic acid, the silica remaining undissolved washed with water, then dissolved in hot solution of potash, and precipitated in the form of hydrate from this solution by an excess of chloride of ammonium. The precipitate, when well washed and still moist, was exposed to a freezing temperature, the ice formed was allowed to thaw, and the hydrated silica, contracted by freezing, well washed with water. It was then triturated with pure cold water (which left no residue on evaporation); by this means it was suspended in the water, forming an opalescent fluid, which, when put upon a filter, furnished a turbid filtrate, which only became perfectly clear by repeated filtration through the same filter. The solution of silica thus obtained was colourless, and did not redden litmus-paper or render turmeric-paper brown even by long action; it was not rendered turbid by muriatic acid, nitric acid, caustic ammonia, chloride of barium and ammonia, or perchloride of iron and acetate of soda. The solution, when boiled and then immediately mixed with acetate or basic acetate of lead, exhibited no turbidity. Nitrate of silver, mixed with so much ammonia that the turbidity first produced had again disappeared, when added to the solution of silica produced no turbidity. Lime-water caused a very slight turbidity in the solution, both when boiled and unboiled; after standing for several hours in a covered glass cylinder, white gelatinous flakes of silicate of lime separated from the fluid; these dissolved again in acetic acid. Lime-water, left standing for the same time close to it in an open cylinder, had only furnished

a slight pulverulent white precipitate. Thus lime-water is the most sensitive reagent for dissolved silica when the absence of carbonic acid has been ascertained.

46·318 grms. of this solution of silica, prepared cold, left on evaporation 0·007 grm. of residue, or 1 part to 6617 parts of solution. But this residue was not pure silica, for when treated with water 0·002 grm. dissolved, and there remained 0·005 grm. of silica, or 1 part of silica to 9264 parts of fluid. This silica dissolved completely in a warm solution of potash, and was precipitated again in white flakes from the solution by chloride of ammonium.

50·000 grms. of the solution were slightly acidulated with muriatic acid, evaporated first in a porcelain and afterwards in a platinum dish, and the residue heated to redness. At the commencement of the calcination the evolution of white fumes was observed, perhaps arising from a small residue of chloride of ammonium. After calcination there remained 0·007 grm. When lixiviated with water, 0·005 grm. of silica remained. This gave 1 part of silica dissolved in 10·000 parts of water. The wash-water produced a strong white turbidity with nitrate of silver; this was insoluble in nitric acid, a proof of the presence of chloride of potassium, the potassium of which must have been combined with the silica in the form of potash.

Hydrated silica, precipitated by chloride of ammonium from a solution of silica in potash, condensed by frost and well washed, consequently retains some potash, and also some ammonia, with obstinacy. It dissolves in pure cold water in the proportion of 1 part of silica to 9264 or 10·000 of water. We may therefore in round numbers take the solubility of such a hydrate of silica at $\frac{1}{10\cdot000}$.

2. Finely triturated siliceous schist was decomposed by hydrate of potash in the humid way, and the mass dissolved in water. The solution was filtered, the filtrate acidulated with muriatic acid and evaporated to dryness, the residue washed first with water containing muriatic acid, and finally with pure water, then dried and calcined. The calcined silica was finely powdered, and poured over with pure distilled water, in which it was left for forty-eight hours, with occasional stirring. The solution, when poured off clear, was examined.

55·159 grms. of this solution left on evaporation 0·002 grm. of dry silica, or 1 part of silica from 27·579 parts of solution.

3. The same calcined silica, left for eight weeks in contact with cold water with occasional stirring, furnished a clear solution, which contained 1 part of silica in 24·966 parts of solution. 249·660 grms. of this fluid furnished on evaporation a white, cracked, nacreous, iridescent film of silica weighing 0·010 grm. This silica also rendered turmeric-paper distinctly, although faintly brown. In this solution of silica lime-water also produced a white flocculent precipitate, soluble in acetic acid, after standing for several hours in covered vessels.

From these experiments it appears that by the treatment of silicate of potash with an excess of muriatic acid, all the potash cannot be got rid of, but that rather a very acid silicate of potash remains, which, even after calcination, is still somewhat soluble in water, in the proportion of 1 part of silica to 24·966 or 27·579 parts of water, or in round numbers of $\frac{1}{25000}$.

The author considers it extremely probable that Struckmann's so-called hydrate of silica, which he precipitated by carbonic acid gas from the aqueous solution of silicate of potash and soda, and treated for a long time with cold dilute muriatic acid, is also a very acid silicate of potash and soda; he is also now of Bischof's opinion, that the silica dissolved in natural waters does not exist as pure silica but as an alkaline hypersilicate.—*Archiv der Pharm.*, cxxxiv. p. 129.

On the Composition of Creosote. By E. von Gorup-Besanez.

In previous memoirs the author had shown that creosote prepared according to Reichenbach's directions from beech-wood tar, is quite a different body from phenylic acid. The author could not hitherto determine the formula of creosote with perfect certainty. The investigation of a series of chlorinated products allowed the formula $C^{26}H^{16}O^{4}$ to be deduced for creosote with a certain amount of probability.

During the time in which the author had been occupied with this investigation, Völckel* also published his investigation of creosote. According to Völckel, creosote prepared by Reichenbach's method is not pure, but contaminated by a small residue of volatile oils, which acquire colour when exposed to the light. Völckel purified his creosote by solution in potash and distillation, and thus obtained a creosote the analysis of which led to the formula $C^{24}H^{14}O^{5}$; a basic lead compound had the composition $C^{24}H^{13}O^{4}, PbO+2PbO$.

The creosote analysed by Völckel dissolved in ordinary acetic acid and in dilute solution of potash, properties which Völckel regarded as a criterion of the purity of creosote. This creosote therefore differs from the author's in many points.

Völckel's creosote contained less carbon and hydrogen than the author's; it had a higher specific gravity (1·076 Völckel, 1·040 Von Gorup-Besanez), and was perfectly soluble in dilute solution of potash and in ordinary acetic acid, whilst the author's was only partially soluble in these menstrua; when Völckel's creosote was heated with lime no colour was produced, whilst the author's became blackish under this treatment. Both however were obtained from wood-tar, the author's from beech-tar, but the wood from which Völckel's was obtained is not stated; they had the same boiling-point, and when boiled exhibited the same phænomena; on distillation with calcined lime, they furnished oils of nearly the same composition.

Völckel regarded the creosote treated by the author as not perfectly pure, because it was not treated with solution of potash. The author has therefore repeated his experiments. He treated 1 lb. of creosote with solution of potash according to Völckel's directions, and separated therefrom 3 to 4 oz. of a product boiling between 395° and 410° F. as pure creosote. This had the following properties:—

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* Chem. Gaz., vol. xii. p. 5.

It was a perfectly colourless, strongly refractive fluid, of an unpleasant odour, but decidedly purer than that presented by the commercial creosote, and somewhat similar to that of guaiacole. Spec. grav. at 55°·4 F.=1·057. With persalts of iron, salts of gold and platinum, with fir-chips moistened with muriatic acid, and with nitrate of silver, it behaved exactly like the creosote investigated by the author, but dissolved completely and readily in dilute solution of potash and in ordinary acetic acid. By long standing in the air it acquires a tinge of yellow, and when dissolved in concentrated solution of potash it becomes slightly brownish, but grows gradually darker and darker until it has attained a dark brown colour. Its analysis gave—

	I.	II.	III.			
C	74·76	74·98	74·85	24 =	144	75·39
H	7·78	7·84	7·78	15	15	7·85
O	17·17	17·48	17·37	4	32	16·76

As this creosote was purified exactly according to Völckel's directions, it is clear that the author's creosote could not be identical with Völckel's. Both crude products however were certainly obtained from wood-tar by Reichenbach's method, whence it follows that the products obtained in this way may vary. According to Völckel, in order to obtain a creosote free from certain volatile oils which contaminate the commercial product, and of the composition found by him, the boiling with solution of potash must be continued until the turbid distillate becomes perfectly clear on the addition of dilute solution of potash; and the solubility of creosote obtained by his method in ordinary acetic acid, and in very dilute solution of potash, is to be regarded as a sign of its purity. The author continued the boiling with solution of potash until the turbid distillate again became perfectly clear on the addition of dilute solution of potash; and creosote, purified by him in accordance with Völckel's method, was readily and completely soluble in very dilute solution of potash and in ordinary acetic acid, but nevertheless it possessed a different composition. Solubility in acetic acid and dilute solution of potash is not a property exclusively belonging to Völckel's creosote.

The result of the author's analyses of creosote, treated with potash according to Völckel's directions, come very near the average of the analyses of creosote not treated with potash.

The author then compares the formulæ to which the previous investigations of creosote have led. The formulæ are $C^{26} H^{16} O^{4}$, $C^{24} H^{15} O^{4}$, and Völckel's $C^{24} H^{14} O^{5}$; and he is of opinion that none of them are to be regarded as rational formulæ for a determinate creosote, but only as empirical formulæ for different products. The author, at least, thinks that the facts furnish a proof, that by Völckel's process of purification two different products are obtained from the crude wood-tar creosote, one of which is of the composition $C^{24}H^{15}O^{4}$ (Von Gorup-Besanez), and the other $C^{24}H^{14}O^{5}$ (Völckel). They are distinguished, as far as we now know, only by the small difference in the specific gravity. The author also obtained a lead compound from his creosote. He mixed the solution with concentrated liquid ammonia, and diluted it with about 200 cub. centims. of water. On the addition of a solution of neutral acetate of lead, also diluted and mixed with a little ammonia, to this solution, a caseous white precipitate, separating in flakes like those of chloride of silver, was produced. This was washed on a covered filter, pressed between blotting-paper, and dried first over sulphuric acid, and afterwards at 212° F. It contained 64·80 per cent. of oxide of lead, which corresponds with the formula $C^{24}H^{14}O^{3}, PbO+2PbO$. But the amount of lead is different according to the mode of treatment; in partial precipitations it was found that the first parts of the precipitate contained less oxide of lead. The lead precipitate loses creosote even at ordinary temperatures, and undergoes a change when dried at a temperature between 176° and 212° F.

Although it appears from this that the creosote investigated by the author was different from Völckel's, the author tried, further, whether his creosote underwent an essential change by repeated treatment with potash. The creosote dissolved completely in potash, without the separation of any body. The boiling was continued for four days, each time five hours, without interruption. The solubility of the distillate in dilute solution of potash could no longer serve to indicate the stopping point, for it was soluble in very dilute solution of potash from the very commencement of the operation.

The distillate of the first day was turbid, exhibited some oil-drops on the surface, and did not acquire any colour by standing in the air. That of the second and third days gradually became violet-purple in the air. This beautiful violet-purple colour was immediately produced when one or two drops of solution of potash were added; a little ammonia (a trace) and perchloride of iron produced a dingy violet turbidity, and afterwards a discoloured one. On the fourth day the distillate was again colourless, and no coloration was produced even by long standing and on the addition of potash; the operation was interrupted, and then the creosote was separated in the same way as the first time, distilled, and freed from water by rectification. The result this time was about an ounce of purified product, the general properties of which agreed with those of the first obtained. Its analysis gave—

C	73·53
H	7·68
O	18·79

These numbers show a diminution of carbon of nearly 1·5 per cent., with a very inconsiderable decrease in the quantity of hydrogen, but still no agreement with Völckel's numbers. The small quantity of material remaining was therefore submitted to another treatment with potash. The phænomena were exactly the same as above. This time also, after about five or six hours' boiling, the peculiar violet-purple coloration of the distillate made its appearance; and its behaviour towards potash and perchloride of iron was the same. After eighteen hours' boiling the operation was interrupted, and the creosote separated and purified exactly in the same way as before. The whole quantity still remaining after rectification amounted only to a few grammes. Analysis gave—

	I.	II.				
C	73·43	73·72	48	=	288	74·03
H	7·72	7·71	29		29	7·45
O	18·75	18·57	9		72	18·52

Thus even by a third treatment of creosote with potash no essential conversion takes place, although the distillates indicate several products of decomposition. By seventy-three hours' boiling, the body $C^{24}H^{14}O^{6}$ was not obtained.

It appears from a comparison of the different analyses of Reichenbach's creosote, that this has no constant composition; in the existing analyses the carbon varies from 75·82 to 71·92, and the hydrogen from 8·16 to 7·10. As these investigations have shown that the creosote becomes poorer in carbon by treatment with potash, it is very probable that the treatment with solution of potash, which is employed in Reichenbach's method, furnishes a different product according as it is continued a longer or shorter time. But whilst Völckel is of opinion that the treatment with solution of potash changes, destroys, and separates certain oleaginous bodies which accompany the creosote, raising its amount of carbon and hydrogen and diminishing its specific gravity, the author thinks that it produces a change of the creosote itself, characterized by the elimination of hydrogen and absorption of oxygen.

At the conclusion of his memoir the author suggests that creosote of the formula $C^{24}H^{14}O^{5}$ may perhaps be still more highly oxidized by continued treatment with potash. By this means, perhaps, guaiacole might be obtained, a body which stands in close relation to creosote. Völckel has adopted for it the formula $C^{15}H^{8}O^{4}$, but the author thinks that from Völckel's analyses the formula might just as well be calculated at $C^{48}H^{25}O^{13}$. We should then have—

$C^{24}H^{15}O^{4}$, the author's creosote after one treatment with solution of potash.

$C^{24}H^{14\frac{1}{2}}O^{4\frac{1}{2}}$, the same after the second treatment.

$C^{24}H^{14}O^{5}$, Völckel's creosote.

$\left.\begin{matrix} C^{24}H^{13\frac{1}{2}}O^{5\frac{1}{2}} \\ C^{24}H^{13}O^{6} \end{matrix}\right\}$, wanting.

$C^{24}H^{12\frac{1}{2}}O^{6\frac{1}{2}}$, guaiacole.

$C^{26}H^{18}O^{2}$, carvacrole (Schweitzer).

Liebig's *Annalen*, xcvi. p. 39.

New Method of preparing Caffeine. *By* M. PUCCETTI.

The modes of preparing caffeine hitherto employed may be reduced, with slight modifications, to the action of acetate and oxide of lead upon the decoction of finely-powdered unroasted coffee. The fluid thus obtained, from which the caffeine is allowed to crystallize, always contains a very large quantity of extractive matter, which, as it is very soluble in alcohol and water, prevents the alkaloid from crystallizing, and thus renders it impossible to extract the whole of the caffeine from the coffee. The author therefore tried the following method. He brought the decoction of coffee to the consistence of an extract, and treated it with alcohol, which left undissolved a resinous substance of the appearance of bird-lime; he then dissolved a slight excess of pulverized caustic lime in the alcoholic fluid, which, when filtered and evaporated to the necessary degree, furnished crystallized, but still impure caffeine. This was pressed between thick linen, to get rid of the adherent mother-liquor, and then dissolved in well-water and treated with animal charcoal, by which means the alkaloid was obtained in a very pure state. This mode of preparation gave one-twentieth of an ounce of caffeine to every pound of coffee, or twice as much as by the ordinary process. As coffee is pulverized with difficulty and does not contain very much of the bitter principle, the author substituted tea for coffee; tea being richer in caffeine, furnishes this alkaloid with more facility and in greater quantity.

Although, by this treatment, tea furnishes a larger quantity of the product, it is certain that the action of the alcohol upon the extract of tea is attended with difficulty, on account of the very large quantity of insoluble matter which it leaves; this not only renders the process inconvenient, but may also lead to a diminution of the result, as indeed the author found to be the case. He therefore changed the mode of preparation in the following manner.

He exhausted the tea by decoction, mixed the fluids obtained, and concentrated them at first with a strong heat. When the fluid was somewhat thickened, he put it into a porcelain dish, and evaporated it by a gentle heat to the consistence of a thick extract. To this extract, whilst still warm, he added 2 oz. of finely-powdered commercial pearlash for every pound of tea; this was stirred in with a wooden spatula. The alkaline carbonate produced a strong effervescence; the mass swelled up, but returned to its original volume at the completion of the reaction. The dish was then removed from the fire, and its contents treated with alcohol; this may be effected in two ways. The alcohol may be added to the substance just taken from the fire, and stirred with a pestle of glass or earthenware, which may be easily done, as the mass is always soft. Or the extract, treated with carbonate of potash, may be taken out of the dish and formed into thin cakes, which are brought to complete dryness on a furnace. In this way a blackish mass of resinous appearance is obtained; it possesses the odour of tea, and is easily powdered. The powder is passed through a hair-sieve, and put into a flask with a ground stopper; alcohol is then poured into it, the flask is closed, kept in a warm place, and shaken from time to time, the alcohol being changed until it no longer exerts any action upon the extract. The alcoholic extracts are mixed together and distilled, and the fluid remaining in the retort is taken out and evaporated in a porcelain dish until it furnishes crystals on cooling. These are pressed between thick linen, dissolved again in well-water, and thus furnish a sufficiently pure theine, which may be obtained very white by treatment with animal charcoal.

The author has employed this process with both green and black tea. The green tea furnished only about half as much caffeine as the black, which confirms the observations of Liebig and others. By the most careful treatment of different kinds of black tea, he obtained very variable quantities of the product, depending of course upon the differences in the quality of the tea. The following are his numerical results:—

Tea employed.	Theine obtained.	Per cent.
4608 grms. green tea..........	38 grms.	0·82
3456 grms. common black tea ..	40 grms.	1·16
3312 grms. the same, another kind	30 grms.	0·90
1584 grms. congou tea	40 grms.	2·55

Archiv der Pharm., lxxxiv. p. 198.

On the Action of Sulphuret of Ammonium upon Paranitraniline.

By A. E. Arppe.

When dinitrobenzole is treated with ammonia and sulphuretted hydrogen, nitraniline is obtained, for which the author some time since proposed the name of paranitraniline. The formation of this body is owing to a decomposition of the sulphuretted hydrogen,—$C^{12}H^4(NO^4)^2$, dinitrobenzole$+6HS=C^{12}H^6, NO^4, N$, paranitraniline$+4HO+6S$.

In this reaction the author observed that, if dinitrobenzole be dissolved in alcohol, and sulphuretted hydrogen be passed into the solution after saturation with ammonia, crystalline scales separate in the course of a short time; these become perfectly white when washed with alcohol. They are completely soluble in alcohol, and consist of hyposulphite of ammonia, NH^4O, S^2O^2.

The red fluid filtered from this deposits much sulphur when evaporated. If the fluid be supersaturated with muriatic acid, a sulphur-yellow precipitate is produced. This body is the new sulphur compound,

Nithialdine, $C^{12}H^8N^2S^4O$.—This body is obtained by extracting the sulphur from the crude precipitate by sulphuret of carbon, and washing the residue with alcohol, and lastly with water. Nithialdine is a product of metamorphosis of paranitraniline; it is consequently produced also by the action of sulphuretted hydrogen upon a solution of paranitraniline saturated with ammonia. After the fluid has been standing for some time in a corked flask, hyposulphite of ammonia gradually separates; when the solution is evaporated, a yellow body is precipitated, and this, when separated from the mother-liquor, which only contains a small quantity of solid residue, is carefully treated with sulphuret of carbon. The insoluble residue is accompanied by a resinous substance, which is extracted by hot alcohol; and in order to get rid of the whole of the hyposulphite, it is finally washed with water.

This body is soluble in a large quantity of concentrated sulphuric acid. It is almost insoluble in water, and even alcohol takes up but an extremely small quantity of it, although when boiled with nithialdine, it acquires a distinct yellow colour. Æther and chloroform have scarcely any action upon it. In acids, except sulphuric acid, it is very difficult of solution. The solution is decomposed by water, and still more completely by alkalies; chloride of platinum produces a reddish-brown precipitate in it, which soon becomes black, and contains about 40 per cent. of platinum. Concentrated potash dissolves it when boiling, but at the same time decomposes it; muriatic acid produces in the alkaline solution a yellow precipitate, which is soluble in an excess of the acid; it is reproduced on the addition of ammonia, and readily acquires a green colour when exposed to the air. The analysis of this body gave—

C	40·27	12	=	72	40·00
H	4·34	8		8	4·45
N	..	2		28	15·55
S	35·45	4		64	35·56
O	..	1		8	4·44

Nithialdine is not produced either from nitraniline, or from nitronaphthalose or nitronaphthalese.—Liebig's *Annalen*, xcvi. p. 113.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Processes for obtaining Sulphate of Soda, Soda, and Sulphuric Acid. By L. Margueritte.

Process for the Preparation of Sulphate of Soda from common Salt and Sulphate of Lime or Magnesia.—Equivalent proportions of sulphate of lead (obtained by roasting galena) and common salt (or chloride of potassium, if it be desired to produce sulphate of potash) are mixed together, and exposed to a strong red heat. The mass fuses, and sulphate of soda and chloride of lead are produced. The latter salt evaporates, and its vapours are condensed in a proper apparatus. After the expulsion of the chloride of lead, the mass remaining is treated with water, when a solution of sulphate of soda is obtained, evaporated, and allowed to crystallize. A certain quantity of sulphate of lead which has not acted is left undissolved. The chloride of lead obtained is triturated, mixed with a solution of sulphate of magnesia, with water containing gypsum or with the solution of any other sulphate, and kept suspended in it by stirring. It is thus decomposed by the sulphate, and becomes converted again into sulphate of lead, with formation of a soluble chloride of calcium or magnesium. The sulphate of lead thus reproduced is collected, freed from the chloride by washing with water, mixed with the sulphate above mentioned as remaining undissolved, and then again employed in the conversion of common salt into sulphate of soda. In this process for the preparation of sulphate of soda, with the exception of the first operation, the sulphuric acid is obtained from gypsum or sulphate of magnesia, or from some other soluble sulphate, and the oxide of lead furnishes the means of transferring the acid from the base with which it was combined to the soda. The sulphate of lead is almost always completely reproduced, only a very small quantity being lost in the washing-water. This however is only the case when the solution of the sulphate with which the chloride of lead is treated is sufficiently diluted. If this solution be concentrated, a considerable quantity of lead remains dissolved in the form of chloride of lead, which arises from the circumstance that sulphate of lead, when in contact with a saturated solution of chloride of calcium, chloride of magnesium, &c., is decomposed by it with formation of chloride of lead. For the conversion of the chloride of lead into sulphate, natural sea-water cannot therefore be employed, because it contains too much chloride of sodium and magnesium.

The calcination of the chloride of sodium with the sulphate of lead may be effected either in retorts or on the hearth of the furnace. In either case the arrangements should be made so that the fusing mass should have a large surface, and but little depth, in order to facilitate the sublimation of the chloride of lead. Care must also be taken that a current of air, or rather of vapour, should pass over the mass to carry the vapours of chloride of lead away with it. In order that this may act sufficiently, the space in which the fusion is effected must be as small as possible. The current of air bears the vapours of chloride of lead into a regular condensation apparatus, which is connected with a chimney to produce the necessary draught.

Process for the Preparation of Caustic Soda or Carbonate of Soda directly from common Salt.—Common salt is mixed with pyrophosphate of lead or zinc, and calcined in the manner above described for the mixture of common salt and sulphate of lead. Pyrophosphate of soda is produced, whilst chloride of lead or chloride of zinc sublimes. The pyrophosphate of soda is dissolved in water, which leaves undissolved a portion of the pyrophosphate of lead or zinc which has not acted. This portion is larger than the quantity of sulphate of lead in the corresponding treatment of that salt. The solution of pyrophosphate of soda is treated with lime, which takes the pyrophosphoric acid and sets free the soda. The solution of soda is separated from the insoluble pyrophosphate of lime, and the soda contained in it may be combined with carbonic acid if it be desired to convert it into carbonate of soda. The pyrophosphate of lime is suspended in water, and treated with the sublimed chloride of lead or zinc, which is thus converted again into pyrophosphate; this is separated from the solution of chloride of calcium, and again employed in the decomposition of further portions of common salt. The same process is applicable to the production of caustic potash or carbonate of potash from chloride of potassium.

According to another proposition of the author's, phosphate of lime may be decomposed by sulphuric acid, and the phosphoric acid obtained employed in the same way as sulphuric acid in the decomposition of common salt; in this way muriatic acid and pyrophosphate of soda are obtained. The latter is dissolved and treated with lime, which sets free the soda and forms pyrophosphate of lime. The phosphoric acid is again separated from the latter by sulphuric acid, and employed in the decomposition of a fresh portion of common salt.

To avoid the employment of sulphuric acid, the following method may be adopted. Phosphate of lead is decomposed by muriatic acid, furnishing chloride of lead and phosphoric acid. By means of the latter, common salt is decomposed, by which muriatic acid and pyrophosphate of soda are produced. The latter is dissolved in water and treated with lime, when it furnishes soda and pyrophosphate of lime. The latter is boiled with water and the chloride of lead previously obtained, by which chloride of calcium and phosphate of lead are produced; and the phosphate of lead is again employed to furnish phosphoric acid for the decomposition of the salt.

Process for the Preparation of Sulphuric Acid from Sulphate of Lime and other Sulphates.—Phosphate of lead is decomposed by muriatic acid; the phosphoric acid thus obtained is mixed with sulphate of lime, and the mass is calcined, when phosphate of lime remains and sulphuric acid is expelled. The phosphate of lime is decomposed by boiling with water and the chloride of lead previously obtained, when phosphate of lead is again produced. This is again decomposed by muriatic acid, and the phosphoric acid set free employed in the decomposition of a fresh portion of sulphate of lime. In this process the muriatic acid is always lost in the form of chloride of calcium; it must consequently always be replaced. But when the sulphuric acid produced is employed in the decomposition of common salt for the production of soda, the necessary equivalent quantities of muriatic acid are always reproduced, with the exception of unavoidable losses. By this process sulphuric acid may also be separated from sulphate of baryta and other sulphates. Muriatic acid may also be obtained by heating chloride of magnesium, which is especially contained in sea-water. This takes place particularly well when the chloride of magnesium is previously mixed with clay, which acts by furnishing the chloride of magnesium at a high temperature with the water necessary for its decomposition into magnesia and muriatic acid.—*Polytechn. Centralblatt*, 1855, p. 1459.

Note on a new Process for arresting the Acid Vapours which escape from the large Chimneys of Chemical Factories. *By* MM. C. *and* A. TISSIER.

This process consists essentially in placing between the principal draught and the great chimney of the manufactory a kind of lime-furnace heated by a contiguous fire, into which the draught of the chimney draws on the one hand the vapours of the manufactory, and on the other the flame of the fire intended to heat the limestone with which the furnace is filled, which requires a certain temperature before the absorption of the gases is complete. The arrangement of the furnace may be varied in any way, but the process consists essentially in the employment of lime or carbonate of lime at such a temperature that the absorption may take place as completely as possible, the increase of temperature assisting at once in the draught of the chimney and the absorption of the acid gases.

This process has been adopted by the authors with excellent results, at their manufactory at Amfreville near Rouen, where the extraction of aluminium has been effected on a pretty large scale, to arrest the acid vapours produced during the manufacture of chloride of aluminium, which are extremely corrosive.—*Comptes Rendus*, Dec. 10, 1855, p. 1045.

Analysis and Preparation of an Alloy for Composition-Files.
By Prof. A. VOGEL.

The metal of the so-called composition-files, which are employed in the application of polishing rouge to small metallic objects, is an alloy of silvery whiteness. These files are used principally by watchmakers for polishing steel pins, and for the production of the deep black polish of some parts of watches. The analysis of a file of this description, of 6 inches in length and 5 lines in breadth, made of a yellowish-white metal, which was very brittle under the hammer, and had a jagged fracture, gave—

Copper	64·4	or 8 parts.
Tin..............	17·6	or 2 parts.
Zinc	8·0	or 1 part.
Lead	8·6	or 1 part.

The author then melted the four metals together under a coat of borax in the above simple proportions. The alloy filled the clay mould well. It is so brittle that it can scarcely be worked with the file; the rods of metal are therefore best ground on a mechanical grindstone to give them the surfaces required for each particular case. The alloy above mentioned gave files of as good quality as that employed for analysis.

The composition is sold at 5 florins per pound. From the price at which the metals required for the alloy are to be bought in small quantities, the pound poured into moulds and ground, may be calculated at 1 florin 12 kr.

The base, by means of which the polishing agents are applied, is of the greatest importance in polishing, and the alloy here described is particularly good. It has probably been obtained empirically by trials.

The author has found that inconsiderable changes in the proportions of the metals exert a great influence upon the usefulness of the alloy.—*Neues Jahrbuch für Pharm.*, iv. p. 138.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Dec. 6, 1855. (Sir Benjamin Brodie, Bart., V.P., in the Chair.)

"On Chemical Affinity, and the Solubility of the Sulphate of Baryta in Acid Liquors." By F. Crace Calvert, Esq.

Solubility of the Sulphate of Baryta.

The author observes that sulphate of baryta is not an insoluble salt, as is generally admitted, for he has found that 1000 grs. of nitric acid, of spec. grav. 1·167, are capable of dissolving 2 grs. of sulphate of baryta; and what renders the knowledge of this fact still more useful in analytical chemistry is, that the insolubility of this salt is affected even by the weakest nitric or hydrochloric acids; for whilst 0·062 gr. of sulphate of baryta only requires 1000 grs. of nitric acid, of spec. grav. 1·032, to hold it in solution, the same quantity of salt requires 50·000 grs. of pure distilled water to dissolve it.

What is not less useful to know is, that the solubility of sulphate of baryta is affected in a higher degree by the bulk of the acid than by its strength. The two following tables, taken from amongst many others contained in the paper, will not only illustrate this fact, but will also give an insight into the way in which the experiments were conducted. The first table illustrates the influence which increasing bulks of the same nitric acid exert on the formation of sulphate of baryta, and the second table the action which increasing strengths of acid have :—

TABLE XVI.

Order of jars.	Number of divisions of the alkalimeter of nitric acid, spec. grav. 1·167.	Number of divisions of the alkalimeter of water added.	Spec. grav. of the bulk of acid.	Sulphate of potash dissolved in the acid.	Nitrate of baryta poured in, previously dissolved in 20 grs. of water.	Time required for a precipitate to appear.	Quantity of sulphate of baryta precipitated.	Quantity of sulphate of baryta dissolved.
1	20	20	1·167	3·34	5·00	3 min.	4·28	Average quantity dissolved equal 0·10 gr.
2	20	40	1·120	...	...	...	4·34	
3	20	60	1·085	...	...	...		
4	20	80	1·067	...	...	...		
5	20	100	1·057	...	...	...	4·35	
6	20	120	1·050	...	...	...	4·35	
7	20	140	1·044	...	...	...	4·36	
8	20	160	1·039	...	...	...		
9	20	180	1·035	...	...	...		
10	20	200	1·032	...	...	...	4·38	

TABLE II.

Order of jars.	Number of divisions of the alkalimeter.	Corresponding weight of nitric acid, sp. gr. 1·167.	Quantity of sulphate of potash.	Quantity of nitrate of baryta.	Weight of sulphate of baryta.	Time required for a precipitate to appear.	Quantity of sulphate of baryta dissolved.
1	40	466·8	3·34	5·00	4·46	Instantly	0·02
2	80	933·6	...	...	...	20 minutes	1·29
3	120	1400·4	...	...	...	2 hours	2·34
4	160	1867·2	...	...	...	8½ hours	3·66
5	200	2334·0	...	...	...	24 hours	
6	240	2800·8	...	...	...	No precip.	
7	280	3267·6	...	...	...		
8	320	3734·4	...	...	...		
9	360	4201·2	...	...	...		
10	400	4668·0	...	...	...		

These tables clearly show the influence which a given strength of nitric acid has on the solubility of the sulphate of baryta; for there is a precipitate in three minutes in all the jars of the first table, whilst we have a precipitate only in the first four jars of Table II.

Another fact which is observed in these tables is, that whilst 240 divisions of the alkalimeter of nitric acid, spec. grav. 1·167, are capable of dissolving, or preventing the formation of, 4·46 grs. of sulphate of baryta, 240 divisions of an acid, of spec. grav. 1·032, only retained in solution 0·086 gr. It follows from these facts, that in future the practice of rendering liquors acid with nitric or hydrochloric acids, must be discontinued when sulphates are to be determined, or separated from chromates, phosphates, &c.

Influence of Mass on Chemical Affinity.

The researches of the author, to illustrate the influence which mass exerts on chemical affinity, are extensive; a few of the results arrived at are here given.

The following table will clearly show the marked influence which increasing volumes of nitric acid have in preventing the formation of sulphate of baryta :—

TABLE IV.

Number of jars.	Number of divisions of the alkalimeter.	Corresponding weight of acid, sp. gr. 1·167.	Quantity of sulphate of potash.	Quantity of nitrate of baryta.	Weight of sulphate of baryta.	Time when precipitate appeared.
1	40	466·8	5·12 grs.	8·00	7·13	Instantly
2	80	933·6	...	...	...	2 minutes
3	120	1400·4	...	...	...	14 minutes
4	160	1867·2	...	...	...	1 hour
5	200	2334·0	...	...	...	1 hour 15 minutes
6	240	2800·8	...	...	...	4 hours
7	280	3267·6	...	...	...	8 hours [cloud)
8	320	3734·4	...	...	...	21 hours (only a
9	360	4201·2	...	...	...	None
10	400	4668·0	...	...	...	None

Thus in this table we perceive, that as the bulk of acid increases, more time is required for a precipitate to appear, although there is a large excess of substance employed on the quantity necessary to give an instantaneous precipitate; and it is curious to observe how wide is the space of time in each successive jar for a precipitate to appear, and in jars numbers 9 and 10 no deposits were formed after twenty-four hours. As the quantity of precipitate decreased rapidly in each successive jar, they were gathered, and their amount determined with due care; and these are the facts observed:—

TABLE V.

Number of jars.	Number of divisions of the alkalimeter.	Corresponding weight of nitric acid, sp. gr. 1·167.	Quantity of sulphate of baryta precipitated.	Quantity of sulphate of baryta dissolved.	Quantity of sulphate of baryta dissolved per 1000 grs.
1	40	466·8	6·86	0·27	0·591
2	80	933·6	5·63	1·50	1·615
3	120	1400·4	4·66	2·47	1·767
4	160	1867·2	3·22	3·91	2·099
5	200	2334·0	2·33	4·80	2·059
6	240	2800·8	1·10	6·03	2·155
7	280	3267·6	0·14	6·99	2·141

The results contained in this table, especially those in the last column, clearly show the influence of mass on chemical affinity, for there is no difference in any of the jars excepting the increasing bulk of the acid; and still we have in jar No. 1 only 0·591 of sulphate of baryta dissolved per 1000 grs. of acid, whilst we have 2·099 in No. 4 jar.

But the relative bulk of acid is not the only influence which affects the affinity of sulphuric acid for baryta, as the relative quantities of nitrate of baryta and sulphate of potash put in presence also exert an action. This fact is illustrated by the following results, taken from three different tables, in which the same quantities of acid were used, but different proportions of salts:—

TABLE IV. E.

Number of table.	Quantities of acid, sp. gr. 1·167.	Sulphate of potash.	Nitrate of baryta.	Sulphate of baryta.	Time before a precipitate appeared.
No. 1	466·8	0·753	1·121	1·00	12 hours
	933·6	0·753	1·121	1·00	None
No. 2	466·8	3·34	5·00	4·46	Instantly
	933·6	3·34	5·00	4·46	2 hours
No. 4	466·8	5·12	8·00	7·13	Instantly
	933·6	5·12	8·00	7·13	2 minutes

This point is again brought out in the following table, which is also taken from several series of experiments :—

Table IV. A.

Number of table.	Order of jar.	Quantities of fluid.	Total quantities of sulphate of baryta susceptible of being produced.	Quantity of acid represented.	Quantities of sulphate of baryta dissolved in 1000 grs.	Increased ratio of solubility.
No. 1	2	933·6	1·00	1000	1·071	0·
No. 2	6	2800·8	4·46	...	1·593	0·522
No. 4	9	4201·2	7·13	...	1·912	0·841

These facts, and others described in the paper, demonstrate that the solubility of the sulphate of baryta, or its non-formation, is not only influenced by the respective bulks of an acid of spec. grav. 1·167, and the respective quality of salts employed, but that the relative quantity of matter put in presence has a decided influence on chemical affinity; and these observations not only corroborate perfectly the results obtained by Mr. Bunsen on the influence of volumes on the combination of gases, and the observations which show a like influence on the carbonates, but also are, I believe, the first instance which has been noticed of irregularity of solubility of a substance in increased multiple bulks of a liquid.

Dec. 13, 1855. (Col. Sabine, R.A., Treas. and V.P., in the Chair.)

"On the Action of Sulphuric Acid on the Nitriles and on the Amides." By G. B. Buckton and A. W. Hofmann, Ph.D., F.R.S.

Although the identity of the nitriles with the hydrocyanic ethers has been established by the experiments of M. Dumas, who obtained them by the action of anhydrous phosphoric acid upon certain ammoniacal salts, chemists have hitherto in vain sought for a method by which a passage might be effected from the nitriles to the general alcohol derivatives.

Our attention has been directed likewise to the same subject, but our exertions, like those of our predecessors, have not yet been crowned with success. The researches on which we have been engaged, have, however, furnished some results which appear to us worthy of the interest of chemists, the reactions being at the same time remarkable for their neatness and susceptibility of general application.

Acetonitrile may be considered as the type of its class, both from the importance of the group to which it belongs, and the facility of its preparation. It is, in fact, the nitrile with which we have been specially engaged. This body when mixed with its own volume of fuming sulphuric acid, evolves a considerable amount of heat, accompanied by a very energetic reaction.

If care be taken to add the acid in small quantities, and to cool the mixture after each addition, scarcely any change of colour is to be observed. By the addition of water, and subsequent saturation with carbonate of barium, a crystalline salt is produced in considerable quantity, which possesses all the characters and composition of the sulphacetate of barium,

$$C_4\,(H_2\,Ba_2)\,O_4\,2SO_3,$$

discovered some time ago by M. Melsens in the mutual reaction of anhydrous sulphuric acid upon glacial acetic acid.

If, on the contrary, the mixture of acetonitrile and fuming sulphuric acid be made rapidly, and the liquid be rather strongly heated, an abundant evolution of carbonic acid indicates a more profound reaction. The residuary mass, which is tough and of a resinous consistency, when treated with water, and boiled with excess of carbonate of barium, yields a magnificent crystallization of a salt represented by the formula

$$C_2\,(H_2\,Ba_2)\,4SO_3 + 4aq.$$

It is a substance of remarkable stability. It does not lose weight at a temperature of 100° C., but four equivalents of water of crystallization are disengaged at 170° C. It is not further affected by a temperature of 220° C. A strong heat resolves it into water, sulphide of barium, sulphurous acid, free sulphur, and carbonic oxide. It may be boiled for hours with fuming nitric acid without the slightest decomposition.

We have also made analyses of the ammonia and silver salts. The former crystallizes with great facility in colourless oblique prisms, which may be readily obtained upwards of an inch in length. They are anhydrous, and perfectly stable at a temperature of 190° C. The composition of this salt is represented by the formula

$$C_2\,[H_2\,(NH_4)_2]\,4SO_3.$$

The silver salt is obtained by digesting oxide of silver with an aqueous solution of the new acid. It forms large crystals, which are easily soluble in water, but insoluble in alcohol or ether. They contain

$$C_2\,(H_2\,Ag_2)\,4SO_3.$$

The acid may be obtained by decomposing either the lead or silver salt by hydrosulphuric acid, or perhaps more conveniently, by carefully precipitating a solution of the barium salt with sulphuric acid. It is an exceedingly soluble and deliquescent substance, crystallizing in long needles. It has a sharp acid taste, with somewhat of the flavour of tartaric acid.

For want of a more convenient name, we propose for this acid the appellation of Methylo-tetra-sulphuric acid. Without wishing to decide at present upon its constitution, its composition allows us to consider it as formed by the association of marsh gas with four equivalents of anhydrous sulphuric acid.

In the reaction of sulphuric acid upon acetonitrile, two distinct phases may be traced. In the first, the nascent acetic acid simply combines with two equivalents of sulphuric acid; in the second phase, the acetic molecule undergoes a more thorough transformation; faithful to its tradition it splits into carbonic acid and marsh gas, which remains combined with four equivalents of sulphuric acid. The new substance also may be regarded as sulphacetic acid, which, losing carbonic acid, has assimilated an equal number of equivalents of sulphuric acid.

The two reactions may be represented by the following equations:—

$$\underbrace{C_4H_3N}_{\text{Acetonitrile.}} + 2HO + 3HSO_4 = \underbrace{C_4H_4O_4\,2SO_3}_{\text{Sulphacetic acid.}} + NH_4SO_4.$$

$$\underbrace{C_4H_3N}_{\text{Acetonitrile.}} + 5HSO_4 = \underbrace{C_2H_4\,4SO_3}_{\substack{\text{Methylo-tetra-}\\ \text{sulphuric acid.}}} + NH_4SO_4 + 2CO_2.$$

The action, then, of bases and of acids upon acetic acid presents a remarkable analogy.

The nature of the change which the acetic molecule suffers, is in fact identical. Under the influence of both agents, it splits into marsh gas and carbonic acid, but in the former case it is the carbonic acid which is fixed, whilst in the latter it is the marsh gas that remains in combination.

The production of methylo-tetra-sulphuric acid calls to mind the interesting substance, sulphate of carbyle, discovered by M. Magnus, by combining olefiant gas with the vapour of anhydrous sulphuric acid. Our new acid is however easily distinguishable from this body, as well by its different composition as by its extreme stability; sulphate of carbyle, as is well known, being decomposed by water into isæthionic acid.

As acetamide differs from acetonitrile only in containing two additional equivalents of water, it undergoes with Nordhausen sulphuric acid a strictly analogous transformation.

From the comparative facility of its preparation it offers peculiar advantages for procuring the methylo-tetra-sulphates. The only difference to be noted is, that in this case the ammonia salt is generally eliminated instead of the free acid.

M. Melsens, in his researches upon the sulphacetates, appears in some sort to have anticipated the existence of the methylo-tetra-sulphates. He remarks that he once found in the mother liquor obtained from the preparation of sulphacetate of silver, a crystalline salt, the composition of which he represents by the formula

$$C_2\,H_2\,Ag_2\,S_4\,O_{12}.$$

It is evident that these crystals contain the same elements as methylo-tetra-sulphate of silver, but M. Melsens does not appear to have investigated the subject further than by showing the existence of this silver salt.

A detailed description of the methylo-tetra-sulphates, and the study of the corresponding bodies of other series, will be on our part the subject of a special memoir.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Occurrence of Inosite, Uric Acid, Taurine, and Leucine in the Tissue of the Lungs. *By* Dr. A. CLOETTA.

IN 1854 the author described a crystalline body which he had prepared from the tissue of the lungs. He was endeavouring to prepare Verdeil's pulmonic acid*, but could find no such body, although 50 lbs. of bullock's lungs were operated upon. He is of opinion that Verdeil's pulmonic acid is nothing but taurine. Together with this he found inosite, uric acid, and leucine.

Fresh, chopped bullock's lungs were left in contact with distilled water for from twelve to eighteen hours at a low temperature. The fluid was then pressed out, and heated with the addition of a few drops of acetic acid in order to coagulate the albumen. The fluid, strained through a fine sieve, was evaporated to one-tenth of its volume on the water-bath, precipitated with solution of acetate of lead, and filtered. The precipitate, which yielded nothing to boiling water, was not further examined. The addition of basic acetate of lead to the clear yellow filtrate produced a voluminous precipitate, from which uric acid and inosite were obtained; the fluid separated therefrom contained principally taurine and leucine, together with considerable quantities of an amorphous matter.

The precipitate produced by basic acetate of lead was washed several times, and decomposed by sulphuretted hydrogen. In the course of twenty-four hours numerous small, white, crystalline grains separated from the fluid filtered from the sulphuret of lead; these had the form of uric acid under the microscope, and were unmistakeably recognizable as such by their behaviour towards acids, ammonia, and fixed alkalies, and by the murexide test.

The fluid separated from the uric acid was evaporated on the water-bath until a sample of it mixed with alcohol became permanently turbid. The whole fluid was then mixed with an equal volume of alcohol, and heated until the disappearance of the turbidity. In the course of a day or two a crystalline mass was deposited upon the bottom and the sides of the vessel; this was purified by repeated crystallization. The crystals produced from a hot, saturated, aqueous solution are rhombic prisms, the obtuse angle of which measures 138° 52′. For their solution they require 6·5 parts of water at 75°·2 F.; they are insoluble in æther and cold alcohol, but dissolve in boiling dilute alcohol, and separate again on cooling in nacreous laminæ. The crystals have a sweet taste; when exposed to the air they effloresce, and become white and opake. At 212° F. the water of crystallization is completely driven off. When carefully heated upon platinum foil, they fuse without acquiring colour, and when rapidly cooled the mass solidifies in a crystalline form; when more strongly heated, they burn without leaving a residue. Concentrated sulphuric acid blackens the crystals when heated; diluted acids and alkalies have no action upon them even at a boiling heat; when heated with a solution of potash and tartrate of copper, a green solution is formed, from which in course of time a light greenish precipitate is deposited, whilst the supernatant fluid again becomes blue; if this be filtered off and again boiled, the same change of colour is observed.

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* Chem. Gaz., vol. x. p. 14.

The substance, dried at 212° F., was burnt with granulated oxide of copper, employing a current of oxygen towards the end of the operation. The analysis gave—

C	40·00	12	= 72	40·00
H	6·71	12	12	6·67
O	53·29	12	96	53·33

The composition of the air-dried compound was—

$$C^{12}H^{12}O^{12}+4Aq.$$

The calculated amount of water is 16·7 per cent.; the amount found 16·5 per cent.

From the analysis and the general properties of this body, it is clear that it is the same as that discovered by Scherer in the muscles, and called by him inosite; its behaviour when heated with nitric acid, ammonia, and chloride of calcium, agreed exactly with Scherer's statements. Inosite may always be easily recognized by these reactions, and by the change of colour observed on boiling it with an alkaline solution of copper. But a very important property of inosite, namely its power of combining with oxide of lead, has hitherto been overlooked; its discovery in, and separation from, animal fluids will be greatly facilitated by this property.

Neutral acetate of lead does not render the solution of inosite turbid; but on the addition of basic acetate of lead, a transparent jelly is produced, which becomes white a few moments afterwards, and acquires exactly the appearance of paste. The author has endeavoured to ascertain the composition of this compound. The precipitate was immediately collected upon a filter, then put into a properly constructed apparatus, and washed in an atmosphere of hydrogen, first with water free from carbonic acid, and afterwards with dilute alcohol. When dried *in vacuo* over sulphuric acid, the compound forms a readily pulverizable mass. It was decomposed by dilute sulphuric acid, the sulphate of lead was long washed with weak alcohol, and the composition of the inosite compound calculated from the weight of the sulphate of lead dried at 212° F. The analysis leads nearly to the proportions $C^{12}H^{12}O^{12}+5PbO$:—

	Found.	Calculated.
Inosite............	23·5	24·4
Oxide of lead......	76·5	75·6

The fluid from the lungs, when precipitated by basic acetate of lead, contains, as already stated, taurine and leucine. To separate these bodies from it, the excess of lead was first of all got rid of by passing in sulphuretted hydrogen, and the filtrate was evaporated on the water-bath to the consistence of a syrup. The residue was very rich in alkaline acetates; and to get rid of these, its solution in weak cold alcohol was precipitated by sulphuric acid, a slight excess of the latter was removed from the filtered fluid by careful addition of baryta-water, and the clear solution evaporated, until an equal volume of absolute alcohol rendered it permanently turbid. The whole fluid was then mixed with alcohol in the above proportion, and heated, when the turbidity disappeared. In the course of a few days, concentrically grouped needles were deposited on the walls of the vessel, and these were purified by recrystallization. When the aqueous solution was slowly evaporated, this body crystallized in rather large glassy prisms; when the cold saturated solution was mixed with alcohol, it separated in delicate needles of several millimetres in length. The crystals were stable in the air, inodorous, and tasteless; they dissolved pretty readily in water, slightly in hot alcohol, but not in absolute alcohol and æther. The aqueous solution showed no remarkable reaction; but the pounded crystals produced a transient reddening of moistened litmus-paper. On platinum foil they burnt away completely; at 212° F. they underwent no alteration in weight; when heated in a glass tube, they decrepitated a little, and then fused with frothing, acquired a black colour, and evolved sulphuretted hydrogen, at the same time smelling like burning hair; by this operation a brimstone-yellow sublimate was formed, and over this colourless oleaginous drops. The amount of sulphur could not be ascertained by boiling the crystals with a concentrated solution of potash to which a drop of acetate of lead had been added. Concentrated sulphuric acid dissolved the crystals with facility; the colourless solution could be heated nearly to the boiling-point of the acid before a slight brown colour was produced. Several experiments which the author made for the preparation of an acid compound led to a negative result.

The form of the crystals, and all their properties, agreed exactly with those of taurine, for the author found that taurine prepared from ox-gall also gave a transient red colour to moistened litmus-paper. But to do away with all doubt as to the identity of the crystals obtained by the author from the fluid of the lungs with taurine, he considered it necessary to determine the amount of nitrogen and sulphur. The following are his results:—

C	..	4	=	24	19·2
H	..	7		7	5·6
N	11·2	1		14	11·2
S	26·4	2		32	25·6
O	..	6		48	38·4

After this there need be no question that the body containing nitrogen and sulphur, which was found by Verdeil in the parenchyma of the lungs, and regarded by him as an acid, is nothing but taurine.

Verdeil, no doubt, observed its behaviour with moistened litmus-paper, and therefore concluded that it was a true acid; that he succeeded in preparing crystallizable salts with it is rendered more and more doubtful, as nothing further is stated regarding them either in Verdeil's paper, which appeared three years ago, or subsequently. It appears consequently that suppositions have been substituted for facts, which in this case is the less excusable, as, on account of its great tendency to combine with bases and expel carbonic acid from the carbonates, Verdeil attributes to his hypothetical pulmonic acid a very important part in respiration.

Glycine certainly stands in near relation to taurine, and the author therefore supposed that it might accompany the latter in the fluid from the lungs. To ascertain its existence, the alcoholic solution from which the taurine had separated was evaporated on the water-bath, the residue boiled with hydrated oxide of lead, the filtrate freed from lead by sulphuretted hydrogen, and evaporated to the consistence of a syrup. The syrup however had no sweet taste, and the author was unable to discover under the microscope any crystals like those of glycine, even after a long time. On the contrary, numerous concentrically-grouped spheres made their appearance, as described by Frerichs and Städeler as characteristic of leucine. Tufted or sheaf-like crystals of tyrosine were also absent.

To isolate the leucine, the syrup was evaporated as far as possible, and extracted by absolute alcohol. The clear solution was evaporated, and the residue, after the leucine had crystallized, was repeatedly pressed between moistened blotting-paper for the removal of intermixed amorphous matter. The residue of pale yellowish leucine was easily obtained pure by recrystallization, and could be unmistakeably recognized as leucine by the woolly sublimate which it furnished when heated in an open glass tube. The quantity obtained was not sufficient for analysis.

As the fluid of the lungs appears to decompose more rapidly than any other animal fluid, and a considerable time had elapsed between the commencement of the operations and the crystallization of the leucine, it appeared possible that this might be the result of decomposition, especially as Frerichs and Städeler found no leucine in the fluids of the lungs of an apoplectic woman. The author therefore repeated his investigations as rapidly as possible, and again found uric acid, inosite, taurine, and leucine, so that the pre-existence of this body in the tissues of the lungs appears to be beyond dispute. The absence of leucine in the lungs of an apoplectic woman might be characteristic of the disease, but it is more probable that the fluid of one human lung is not sufficient for its detection with certainty, as it occurs in but small quantity in the fluid of the lung of the ox. —*Verhandl. der Naturb. Gesellsch. zu Zurich*, iv.

On the Anilide Compounds of Malic Acid. By A. E. Arppe.

By the mutual action of aniline and an acid assisted by heat, there is a simultaneous production of anile from 1 equiv. aniline

+1 equiv. acid—2 equivs. water, and of anilide from 1 equiv. aniline+2 equivs. acid—4 equivs. water. For the production of these compounds, it is therefore best to employ 2 equivs. aniline to 3 equivs. acid.

A mixture of aniline, $C^{12}H^7N$, and malic acid, $C^4H^3O^5$, in these proportions, when heated to fusion and kept gently boiling for two hours, furnished a brown syrup, which solidified on cooling, and from which both bodies were abundantly obtained.

By boiling with water, a slightly coloured solution and a strongly coloured residue are obtained; the former contains malanile and the latter malanilide.

Malanilide, $C^{16}H^8NO^3$, is obtained by dissolving the undissolved residue in boiling alcohol, and setting it to cool. The compound crystallizes, and when purified forms colourless, slightly shining crystals, which fuse at 347° F., with partial decomposition; the greater portion is volatilized undecomposed, and when ignited burns with a luminous smoky flame.

This body is $C^{12}H^7N+C^4H^3O^5-2HO=C^{16}H^8NO^3$. With the assistance of heat, malanilide dissolves in sulphuric acid; muriatic acid, ammonia, and dilute solution of potash do not dissolve it more abundantly than water. It is rather difficult of solution in alcohol and æther. Its analysis gave—

C	67·66	16	=	96	67·61
H	5·70	8		8	5·63
N	...	1		14	9·86
O	..	3		24	16·90

Conversion of Malanilide into Tartanilide.—The behaviour of this amide with boiling concentrated solution of potash is remarkable. The greater part of it is decomposed and taken up by the potash, whilst a greasy body is separated on the surface. If water be added to the mass, the semi-fluid substance is converted into a white powder, which is obtained quite free from alkali by washing with water. The analysis of this body gave—

C	64·17	16	64·00
H	5·41	8	5·33

These numbers correspond with the formula of tartanilide, $C^{16}H^8NO^4$. As the properties of this body also agree with the results obtained, the malanilide must have been converted into tartanilide. This is not effected by mere oxidation, but a portion of the malanilide is decomposed by the potash, and the conversion is therefore the consequence of a decomposition, and not of a mere oxidation.

Malanile, $C^{20}H^9NO^6$, is obtained from the solution above described by evaporation; it forms at first a granular mass, still mixed with some malanilide. It is purified by recrystallization, or by treatment with animal charcoal. It crystallizes with facility, and separates from its concentrated aqueous solution in fine needles, which are also produced by the concentration of its alcoholic solution. It usually forms nacreous laminæ; if the solution be much diluted, it forms rectangular prisms. Malanile dissolves in water, alcohol, and æther. It fuses at about 338° F., and when heated between two watch-glasses furnishes a fine mealy sublimate. The formation of this body results according to the equation $C^{12}H^{7}N + C^{8}H^{6}O^{10} - 4HO = C^{20}H^{9}O^{6}$. Analysis:—

C	62·80	20	=	120	62·83
H	4·77	9		9	4·71
N	..	1		14	7·33
O	..	6		48	25·13

When boiled with aqueous ammonia, malanile furnishes malanilic acid, which forms with ammonia a granular salt, crystallizing with difficulty. This salt, treated with baryta-water, furnishes the baryta-salt in the form of a precipitate, and this, when decomposed by dilute sulphuric acid, gives a solution of malanilic acid; but if the sulphuric acid be in the least excess, the malanilic acid is again converted into malanile.

Malanilic Acid, $C^{20}H^{11}NO^{8}$, crystallizes in slightly shining, white, crystalline grains, composed of small needles; it has a distinct acid taste and reaction, fuses at about 293° F., and dissolves in water, alcohol, and æther.

The malanilates are distinguished by their solubility in water; the solution of the ammoniacal salt, when mixed with lime-water, remains clear. In this solution acetate of lead produces a precipitate of a fine yellow colour, which is soluble in water.

Malanilate of baryta dissolves in considerable quantity in water; it crystallizes in snow-white masses of crystals, and is insoluble in solution of muriate of ammonia. Malanilate of silver forms a white precipitate, which is readily reddened by exposure to daylight; it is soluble to a considerable extent in water, and may be obtained in shining crystalline laminæ.

When dissolved in nitric acid, malanile appears to form a nitromalanile.—Liebig's *Annalen*, xcvi. p. 106.

On Crystallized Acetate of Magnesia. *By* KARL VON HAUER.

Acetate of magnesia is mentioned in all the text-books of chemistry as a salt which is crystallizable only with great difficulty; and when its aqueous solution is evaporated, generally remains in the form of a bitter, sticky, and deliquescent gum. In the dehydrated state, according to the analyses of Wenzel and Richter, its constitution is $C^{4}H^{3}MgO^{4}$. According to Connell, it is distinguished from formiate of magnesia by its incapability of crystallization and its deliquescence.

The author prepared this salt by dissolving caustic magnesia in acetic acid. If the aqueons solution thus obtained be evaporated, it will become concentrated until it attains the consistence of a syrup, and will at last become dry, without presenting any formation of crystals. This is the case even when the evaporation is effected by a moderate heat. But if the concentrated solution of the salt be left to evaporate spontaneously at the ordinary temperature of a room, it generally acquires a crystalline film on the surface, which gradually becomes very solid, and so close that it to a certain extent hermetically seals the solution, and consequently prevents its further evaporation. It is but rarely that crystallization commences at the bottom of the vessel, and the surface of the fluid remains always free, but under these circumstances the largest crystals are obtained. This mode of preparation however depends almost entirely upon chance. The author therefore tried concentrating the solution of the salt very strongly by heat, and then letting it cool as slowly as possible. In this way he always succeeded in obtaining crystals of considerable size, especially when a large volume of fluid was employed, this greatly facilitating the slow cooling. The formation of crystals takes place in this case with acid, as well as with more neutral solutions. The author did not succeed in adding to the size of ready-formed crystals, because when these were placed in freshly-concentrated solutions they became crusted with a new formation of small crystals, without increasing in their original form. Solutions containing an excess of acid furnish more distinctly-developed crystals, with bright shining surfaces; those formed in more neutral solutions are larger, but generally less transparent. The salt obtained is not so very deliquescent as is generally supposed. At the ordinary temperature of a room the crystals may be readily dried on blotting-paper, and they exhibit no alteration even when kept for months. In closed vessels they may be kept with still less danger of deliquescing. The composition of the salt was found to agree with the formula $C^4 H^3 MgO^4 + 4HO$. Its analysis gave 18·73 and 18·75 per cent. of magnesia, which was determined by the calcination of the salt.

For the purpose of this analysis, the salt was dried at the ordinary temperature of the room. An analysis of crystals which had already been kept for some months gave the same results. When dried over sulphuric acid, the salt effloresced. When heated on the water-bath, it lost its 4 atoms of water of crystallization almost entirely; but this required a considerable time. The loss of weight, whilst drying at 212° F., took place as follows:—

1·115 grm.	weighed after	4	hours	0·907	grm.	=18·65	per cent. loss.
...	..	9	...	0·837	...	=24·93	...
...	...	15	...	0·783	...	=29·77	...
...	...	19	...	0·766	...	=31·30	...
...	...	24	...	0·750	...	=32·73	...

It appears also that when this heat is so long continued, a certain, although very small quantity of acetic acid is expelled with the water, for when the salt dried in this manner was dissolved in water, it left a small residue. When more strongly heated, it behaved like the other acetates, first losing its water and swelling up strongly, evolving acetic acid and afterwards acetone, and finally smouldering away when heated to redness. Its crystals belong to the monoclinohedric system.—*Jahrb. der K. K. Geolog. Reichsanstalt*, 6 Jahrg., p. 136.

On the Compounds of Stibamyle. By F. BERLÉ.

Stibtriamyle.—The alloy of antimony and potassium, Sb^3K, is prepared according to Löwig's directions. From 2½ to 3 oz. of it are reduced to a fine powder, and mixed with about half the volume of fine sand. The mixture is then put into a flask, and iodide of amyle is poured over it until it is thoroughly soaked. When heated a little, a violent action takes place, and the excess of iodide of amyle distils over, and is allowed to flow off through a gas-tube. When no more iodide of amyle passes and a white vapour appears in the neck of the flask, the latter is to be corked up tightly and left to cool. The mass is then softened with water, and put into a spacious cylinder filled with carbonic acid. In this the mass is extracted with æther as long as the latter acquires a yellow colour, and on burning a sample a white vapour of oxide of antimony makes its appearance. The solution is then put into a cylinder completely filled with carbonic acid, a little water is added to it, and it is carefully distilled.

Pure stibtriamyle forms a transparent slightly yellow fluid. When cold, up to 68° F. it is very thick, but at a higher temperature it flows readily. In contact with atmospheric air, it fumes very strongly, but does not inflame; it is decomposed, and deposits a white powder. Its odour is peculiarly aromatic; its taste bitter, somewhat metallic, and very persistent. If a drop of it be let fall upon a piece of blotting-paper, it produces so much heat during its oxidation, in consequence of its great diffusion on the surface and in the pores of the paper, that the fibres of the latter are carbonized but not ignited. It is remarkable that a contamination of 2 per cent. of amylic alcohol or iodide of amyle is sufficient to deprive it of this property; it is decomposed, but without fuming or any remarkable evolution of heat. It is insoluble in water, and may therefore be easily kept under water; it dissolves with difficulty in absolute alcohol, more readily in æther and alcohol, and very easily in æther. It nevertheless communicates its odour and taste to any of these fluids with which it may have been in contact even for a short time. Its specific gravity is 1·1333 at 30°·6 F.

When heated with iodide of amyle in a sealed glass tube on the water-bath, it did not present the smallest trace of any combination with it even after eight days. Its analysis gave—

Sb	53·55	52·56	51·66	1	=	129	37·72
C	10·00	10·00	10·00	30		180	52·63
H	..	..	..	33		33	9·65

By the above process stibtriamyle is not always obtained pure; it often contains undecomposed iodide of amyle and amylic alcohol. The silver compounds serve best for its purification, as these form, together with insoluble haloid compounds, well-crystallizable salts. Stibtriamyle contaminated with amylic alcohol is converted into the bromide by the addition of an alcoholic solution of bromine. In this way perfectly neutral bromide and iodide may be easily prepared. If a strong solution of bromine or iodine be first added to the radical dissolved in æther and alcohol, and then gradually changed to one more and more diluted, a little care will enable us to find the exact point of decolorization of the bromine or iodine as easily as the change from a wine-red to a brownish-red in alkalimetric experiments. On the addition of a large quantity of water, the bromide, which is insoluble in that fluid, was thrown down, whilst the greater part of the amylic alcohol remained dissolved in the very dilute alcohol thus produced. This was separated from the compound by decantation, and the latter was then converted into the oxide by means of suspended oxide of silver. The oxide was separated from the bromide of silver formed and the excess of oxide of silver by filtration, and then thrown down by water; by this means it lost a further portion of the amylic alcohol, so that the chloride obtained by dissolving the oxide in muriatic acid and alcohol and repeated precipitation by chlorine, was entirely free from it, and only contained a little water. To get rid of this, it was heated for a long time on the water-bath, and dried over chloride of calcium. It was then perfectly pure. The radical, when contaminated by iodide of amyle, could be purified in a similar manner.

Oxide of Stibtriamyle, $Sb(C^{10}H^{11})^3O^2$.—If stibtriamyle be dissolved in æther, and the solution be allowed to evaporate slowly, the residue is a grayish-yellow, very tough, resinous mass, which is rendered a little more mobile by heat, but readily decomposes at a high temperature. Its taste and odour are similar to those of stibtriamyle itself, but the odour is more aromatic. It is insoluble in water, difficult of solution in aqueous alcohol and in æther, but dissolves readily in absolute alcohol. The heavy metallic oxides are precipitated from their salts by its alcoholic solution. It dissolves readily both in the oxyacids and the hydracids; the compounds produced may be thrown down from their alcoholic solutions by water.

Protochloride of Stibtriamyle, $Sb(C^{10}H^{11})^3 2Cl$.—This compound is best prepared by dissolving the oxide in muriatic acid. It appears as a yellowish fluid, diaphanous but not transparent; it is thickly fluid at ordinary temperatures, and is rendered more fluid by heat. Its specific gravity is greater than that of water. It is soluble in alcohol and æther, but dissolves best in absolute alcohol. Water precipitates it from its alcoholic solutions, but nevertheless a little water and alcohol always adhere to the compound, and can only be got rid of by boiling for hours on the water-bath and long drying over chloride of calcium. Its odour and taste are peculiar, but similar to those of the radical. It cannot be distilled without change, but becomes decomposed at a temperature above 320° F. The products of decomposition however take some of it up, and carry it over with them.

The *protiodide* and *protobromide*, $Sb(C^{10}H^{11})^3, 2I$, and $Sb(C^{10}H^{11})^3, 2Br$, are obtained in the same manner; they both agree very closely in their properties with the preceding.

Nitrate of Stibtriamyle, $Sb(C^{10}H^{11})^3 O^2 + 2NO^5$.—When a solution of nitrate of silver in alcohol is added to the chloride or iodide of stibtriamyle as long as a precipitate is produced, and the mixture is filtered, the filtrate contains an emulsion, from which, after standing some time in a warm place, two fluids separate; these are a pale yellow and very mobile oil and a poppy-red oil, which collects at the bottom of the vessel. If the upper fluid be poured away and left to evaporate slowly, fine, thin, white, silky crystals, grouped in a stellate form, separate after some time. To obtain them pure, they must be again dissolved in dilute alcohol, recrystallized, pressed between blotting-paper, and lastly dried under the air-pump. The dark red oil also dissolved in a large quantity of aqueous alcohol, and deposited crystals after long standing. These fused at a very low temperature (about 68° F.), and in the fused state they did not dissolve in alcohol so readily as when they were brought in contact with it in the crystalline form. Their proper solvent is aqueous alcohol, and they are insoluble in water and æther. Their taste is peculiarly metallic. They are the only crystallizable compounds of stibtriamyle.

Sulphate of Stibtriamyle, $Sb(C^{10}H^{11})^3O^2+2SO^3$.— When equivalent proportions of a haloid compound of stibtriamyle and sulphate of silver are mixed together, the sulphate of stibtriamyle is obtained in the alcoholic solution, whilst iodide or chloride of silver is precipitated. This compound does not crystallize, but forms an oil similar to the fused nitrate. The two salts are also very similar in their other properties, and can only be distinguished by chemical reagents.

Oxide of Stibtriamyle and Antimony.—When stibamyle is left standing in the air, it fumes strongly, and lets fall a white powder. This is insoluble in æther, alcohol, and water, and may consequently be collected on a filter, and washed with æther and alcohol. This operation takes a long time, as it is only freed with difficulty from the oxide of stibtriamyle, which always adheres to it. When dried at 212° F., it forms a white laminar powder, which cannot be further reduced in the mortar, without adhering to the sides so firmly that it cannot be again removed. It does not dissolve in muriatic acid, and but very imperfectly in fuming nitric acid; nitromuriatic acid dissolves it, but takes a very long time in doing so. At first black carbonaceous bodies separate, but these disappear after long digestion. The substance is very stable, and remains long without alteration at a high temperature; it is only decomposed at a red heat, when carbon is separated, and an antimonial speculum is deposited in the cooler part of the tube in which it is heated.

This body appears to be $Sb(C^{10}H^{11})^3O^2+2SbO^3$, corresponding with the compound of oxide of stibæthyle and antimony, $Sb(Ae^3)^3$, O^2+2SbO^3.

Basic Sulphostibtriamyle and Protosulphuret of Antimony, $Sb(C^{10}H^{11})^3S^2+2SbS^3$, is produced when sulphuretted hydrogen is passed through the alcoholic solution of the preceding salt. A white powder is thrown down at first, and this becomes yellow, and afterwards of an orange colour. When dry, the precipitated body is a brownish-yellow powder, which is insoluble in æther, alcohol, and water. It is only decomposed by a very high temperature, and then behaves like stibtriamyloxide of antimony, except that, besides antimony, sulphur is also sublimed. When fuming nitric acid is poured over it, the compound ignites, and burns with the same beautiful, intense, tawny light that is observed in the combustion of finely divided antimony in oxygen. A black body separates in this operation, but is again dissolved by twenty-four hours' digestion in nitromuriatic acid. In this solution all the sulphur exists as sulphuric acid, so that when the fluid has been diluted with alcohol and water, it may be precipitated by ClBa and determined.

Stibbiamyle, $Sb(C^{10}H^{11})^2$.—In the distillation of the alloy of antimony and potassium with iodide of amyle and stibtriamyle, when the distillate was passed into a small flask standing in a large cylinder filled with carbonic acid, and through which a current of carbonic acid was constantly passing, it could be distinctly ascertained how long iodide of amyle was forming by the amount of heat set free in the distillation-tube; from the moment when the metallic radical passes alone the tube suddenly becomes cold, as these radicals take up but little heat in changing from the fluid to the gaseous state, and can therefore only set free a very little when the process is reversed. Immediately on the occurrence of this cooling of the distillation-tube, the cylinder was turned so as to bring the mouth of the tube over another flask filled with powdered alloy of antimony and potassium and quartz-sand. The flask, which was at first but gently heated, must now generally be exposed to a stronger heat, which is gradually raised at last to a dull red heat. When the contents of the flask appeared as a dry dusty powder, and no fluid could be seen to pass even at the strongest heat, the distillation was interrupted and another flask substituted. In order to convert the last traces of iodide of amyle which had passed over into the metallic radical, the whole fluid was again distilled over alloy of antimony and potassium.

The distillate thus obtained consisted of a mixture of two bodies, which the author separated by fractional distillation. Thus in water of 176° F. a gas distilled off, which ignited in the air, and burnt with the strongly luminous flame of a carburetted hydrogen gas containing much carbon, and with diffusion of a white vapour of oxide of antimony. When it had been kept for about eight weeks over water, it no longer presented this antimonial odour; it only burnt with a strongly luminous, and not sooty flame. In the interior of the small bell-glass in which it had been kept this time, a white coating was distinctly visible; when shaken with muriatic and tartaric acids, it disappeared, and the fluid then exhibited all the reactions of antimony. The gas consequently consisted of antimony, carbon, and hydrogen. It is perhaps the body $Sb(C^{10}H^{11})$.

The residue freed from this gas was a greenish-yellow, rather mobile fluid, of a peculiarly aromatic odour and a bitter taste. It is insoluble in water, but mixes with strong alcohol and æther in all proportions. It does not fume in the air; when dropped upon paper, it neither ignites nor carbonizes it. When ignited, it burns with a strongly luminous flame, with diffusion of a white vapour of oxide of antimony. When heated in pure oxygen gas, it explodes with the greatest violence. Fuming nitric acid decomposes it with a very considerable evolution of heat. It sinks in water, and is therefore specifically heavier than it. Its analysis gave, in accordance with the above formula,—

Sb	..	..	..	1	=	129	47·6
C	45·13	43·30	44·83	20		120	44·3
H	8·80	9·01	8·60	22		22	8·1

Carbonate of Stibbiamyle, $Sb(C^{10}H^{11})^{3}, O+CO^{2}$.—During the evaporation of the ætherial solution of stibbiamyle in the air, it attracts oxygen, and becomes converted into oxide. This also at the same time attracts carbonic acid, and the carbonate is thus formed. It behaves exactly like the oxide, but forms a very tough, scarcely mobile mass, which cannot be poured from one vessel into another. It only becomes more fluid at 158° to 176° F. Its analysis gave 42·9 of carbon; calculation requires 41·52.

The haloid compounds of stibbiamyle all appear to form uncrystallized sticky fluids, with the properties of the carbonate. The oxysalts, on the contrary, appear to be solid, amorphous, pulverulent bodies, which are also precipitated by water from their alcoholic solutions in a slimy form, but after long standing they may be filtered, and dry on the filter, forming bodies of the above-mentioned properties. Their odour and taste are nearly the same throughout. They do not dissolve in water or dilute alcohol, and with difficulty in æther; absolute alcohol is their proper solvent.—*Journ. für Prakt. Chem.*, lxv. p. 385.

On the Incandescence of Metal Wires in Alcoholic Vapour.

By H. REINSCH.

Reinsch long since showed* that wires of all the infusible metals, as also most of the metallic oxides, continued incandescent in the vapour of alcohol, so that this property is by no means peculiar to platinum. He has had the opportunity of making some experiments upon this phænomenon, which have led him to a remarkable observation. When a spiral of copper wire is fastened in the manner described by Reinsch upon the wick of a spirit-lamp, and the lamp is lighted and then quickly blown out, the copper wire continues incandescent just as well as platinum. This incandescence, however, only lasts two to three minutes. But if a small fragment of coke be inserted into the spiral and the whole be brought to a red heat, the wire will continue to glow permanently after the extinction of the flame. The author attempted to explain this phænomenon by the supposition that the high temperature was better maintained by the fragment of coke, as it does not carry off the heat so quickly as the wire, and as it were forms a sponge, which always retains sufficient heat to communicate to the wire the temperature necessary for its incandescence. This supposition, however, was not confirmed, as the spiral was not extinguished even when the piece of coke was removed. If it be then blown out and again ignited, it continues to glow without the piece of coke, so that by contact with the coke it has passed into a peculiar state, which, in the author's opinion, must arise from an electrical action between the two substances.—*Archiv der Pharm.*, cxxxiv. p. 187.

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* Chem. Gaz., vol. iv. pp. 158, 315.

On Alloxanic Acid. By G. STÆDELER.

To prepare alloxantine from the mother-liquor obtained in the preparation of alloxan by means of nitric acid, Schlieper* recommends the neutralization of the free acid with chalk before the employment of sulphuretted hydrogen, in order to prevent an oxidizing action. With sufficient care this process is certainly a very good one; but if the nitric acid be completely saturated with chalk, bicarbonate of lime is produced at the same time, and this quickly converts the alloxan into alloxanic acid.

This behaviour of bicarbonate of lime may be employed with advantage in the preparation of alloxanic acid. If the dilute acid mother-liquor be saturated with an excess of chalk, binalloxanate of lime separates immediately, partly on the surface of the fluid and partly as a precipitate, forming well-developed crystals, or crystalline crusts; from these the chalk may be easily separated by suspension in water. It is advisable to use a considerable excess of chalk, and to stir the mixture frequently, as then the formation and separation of the salt is soon completed. To purify the heavy crystals remaining after the treatment with water, they were dissolved in water nearly at a boiling heat, and the solution, filtered whilst hot, deposited the alloxanate of lime in white crusts on cooling.

Remarkably beautiful crystals are often found in the froth formed during the saturation of the mother-liquor with chalk. They are perfectly transparent, glassy, oblique, six-sided columns, in which however two of the sides are usually so slightly prominent that the crystals look like pointed rhombohedra. In dry air they immediately lose a portion of their water of crystallization, and become milk-white, so as to prevent their being measured.

According to Schlieper, binalloxanate of lime consists of $\left.\begin{matrix}CaO\\HO\end{matrix}\right\}C^8H^2N^2O^8+5Aq$. It loses all its water of crystallization at ordinary temperatures over sulphuric acid, and also at 212° F.; it appeared therefore that the determination of the amount of water of crystallization would be the most simple method of ascertaining the identity of the crystals obtained by me with the alloxanate obtained in the ordinary manner. My determinations of the water differed essentially from Schlieper's, and I was therefore under the necessity of making a complete analysis of the salt.

Air-dried, perfectly transparent crystals lost on the average of three determinations 4·25 per cent. of water over sulphuric acid; they became milk-white and opake.

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* Chem. Gaz., vol. iv. pp. 1, 96, 110.

At 212° F. the milk-white salt lost 19·7 per cent. of water on an average of two determinations. The analysis gave—

	Found.			Calculated.
Ca	12·59	1	= 28	12·50
C	21·12	8	48	21·43
H	3·63	8	8	3·57
N	12·72	2	28	12·50
O	49·94	14	112	50·00

From this composition we obtain the same formula as that established by Schlieper for the air-dried salt. 5 equivs. of water of crystallization amount to 20 per cent.; found, 19·7 per cent.

The colourless dry salt contained 1 equiv. more water, and is $\left.\begin{matrix}CaO\\HO\end{matrix}\right\} C^8H^2N^2O^8+6Aq$. It loses this completely over sulphuric acid. From calculation the loss ought to be 3·86 per cent.; 4·25 per cent. were found. When the binalloxanate of lime crystallizes from the hot saturated aqueous solution, the salt is not perfectly transparent, and the amount of water of crystallization is between 5 and 6 equivs. Over sulphuric acid such crystals lose from 2 to 3 per cent. of water.

Free alloxanic acid may easily be obtained from the lime-salt. The concentrated solution, supersaturated with ammonia, is precipitated by carbonate of ammonia; the solution is heated, and the carbonate of lime separated by filtration. The separation of the carbonate of lime is not complete in the cold. To get rid of free ammonia, the filtered solution of the ammoniacal salt is placed for some time over sulphuric acid; it is then precipitated by acetate of lead, and the precipitate is washed. The lead-salt is free from ammonia; it is suspended in alcohol whilst still moist, and decomposed by sulphuretted hydrogen, when the alcoholic solution of alloxanic acid may be evaporated by a gentle heat. The alloxanic acid remains in the form of a colourless tough mass, which gradually becomes crystalline. Schlieper is of opinion that the amorphous state of the acid is produced by exposure to too high a temperature during the evaporation of the solution; but I also obtained it in an amorphous state at first, when the alcoholic solution was allowed to evaporate at the ordinary temperature over sulphuric acid.—Liebig's *Annalen*, xcvii. p. 120.

Note on the Preparation of Uranium. By E. Peligot.

In 1842 the author showed, that by treating protochloride of uranium with potassium, uranium was obtained partly in the form of a black powder, and partly in silvery metallic plates; but as the sudden elevation of temperature produced by the reaction prevented the employment of earthen crucibles, and rendered the use of platinum vessels necessary, the metallic scales were always alloyed with platinum.

Since sodium has been so easily procurable, the author has renewed his experiments, substituting sodium for potassium. He proceeds in the following manner:

The quantity of sodium necessary to decompose the green protochloride of uranium (prepared by submitting one of the oxides of this metal to the simultaneous action of chlorine and charcoal) is put into a glazed porcelain crucible. The sodium is covered with very dry chloride of potassium, and then with a mixture of the latter salt and chloride of uranium. The crucible, closed with its lid, is placed in a luted earthen crucible, which is filled with charcoal-powder, and also closed with an earthen cover. The object of the addition of chloride of potassium is to render the reaction less instantaneous and violent.

The crucible is heated until the reaction takes place, which is known by the sound produced at that moment; it is then immediately removed into a blast-furnace, and kept at a white heat for a quarter of an hour or twenty minutes; on cooling it, a fused cinder is found in the porcelain crucible, and this encloses several globules of uranium.

Thus prepared, uranium possesses a certain degree of malleability; it is hard, but may easily be scratched with steel; and its colour resembles that of nickel or iron. In the air it acquires a slight yellowish tint, in consequence of a slight oxidation of the surface. When heated to redness, it exhibits a brilliant incandescence, and becomes covered with a voluminous black oxide, in the interior of which a portion of the metal is found unchanged if the action of heat has been stopped in time. Its density is 18·4, so that next to platinum and gold it is the heaviest body with which we are acquainted. This specific gravity may perhaps justify the high equivalent which the author has attributed to this metal.

The author has also ascertained that uranium may also be obtained from the same green chloride by means of aluminium. Its isolation by this reaction is no doubt due to the great volatility of the chloride of aluminium.—*Comptes Rendus*, Jan. 21, 1856, p. 73.

Deposition of Arsenious Acid in Commercial Oil of Vitriol.

By J. CAMERON, F.C.S.*

I observed a crystalline deposit, some time ago, in several bottles of commercial sulphuric acid which had stood in the laboratory for five or six years, the sides and bottom of the bottles being in a great measure incrusted over. On examining these crystals under a lens, I found them to be octohedra; and on further testing them by the blowpipe, hydrosulphuric acid, and Reinsch's test, I found them to be crystals of arsenious acid. I should say that more than an ounce of arsenious acid was deposited in each of the bottles, containing about 8 lbs. of vitriol in each of them. This acid in all probability has been manufactured from very impure iron pyrites; otherwise so much arsenious acid would not have been present. It is very problematical, even after adopting the various methods of purifying, if this acid could be freed from such a considerable proportion of arsenic.

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* Communicated by the Author.

Spitty Copper Works, South Wales.

On the Identity of Sanguinarine with Chelerythrine.

By Dr. James Schiel.

The author has ascertained by analysis that sanguinarine and chelerythrine are one and the same substance. Both bodies have the composition $C^{38}H^{16}NO^{8}$. This formula has 1 equiv. more carbon than that first given by the author for sanguinarine. For the preparation of this body the author extracts the root of *Sanguinaria Canadensis*, or that of *Chelidonium majus*, with water acidified with sulphuric acid, and precipitates the extract with ammonia. The precipitate is washed with water and dissolved in æther, the solution is heated with animal charcoal, and the sulphate of the alkaloid is thrown down from it by the addition of sulphuric acid diluted with æther.—Silliman's *Journal*, 2 ser. xx. p. 220.

On the Composition of Hæmatoidine. *By* C. Robin.

The author obtained a quantity of 3 grms. of hæmatoidine, which had separated in a crystalline form in a cyst of the liver (*cyste hydatique de foie*). The red colouring matter of the blood, which Chevreul called hæmatosine in 1827, and which has since generally received the name of hæmatine (previously employed by Chevreul for the red colouring matter of log-wood), is not crystallizable; but whenever an effusion of blood takes place in the tissues of an organism, microscopic crystals are formed in from four to twenty days; these were called hæmatoidine by Virchow in 1847.

Hæmatoidine forms needles or obliquely-rhombic prisms; they are rather hard and triturable; under the microscope they refract the light strongly; they are of an orange-red or poppy colour, and carmine-red towards the centre and at the edges. In reflected light they appear of a beautiful red colour, like alizarine or iodide of mercury. The angles of the prisms are 118° and 62°.

When heated, they first give off an odour of tar, and afterwards that of azotized matters; they then ignite, burn like a taper, and leave a voluminous coal. When the air is excluded, bad-smelling gases are evolved, a tar is formed, and a bulky cinder is left.

The substance does not dissolve in water, alcohol, æther, glycerine, or acetic acid; it dissolves readily in ammonia with an amaranth-red colour, which soon passes to saffron-yellow, and lastly to brown. Potash and soda cause hæmatoidine to swell up, decompose it, and dissolve it by degrees in small quantity when compared with ammonia; the solution is reddish.

Nitric acid dissolves this substance with a dark red colour; gas-bubbles are formed when the solution is concentrated. Muriatic acid dissolves it in small quantity, and the solution is yellowish-red. The remaining crystals appear yellowish-red under the microscope; by reflected light they are ochre-yellow. Sulphuric acid does not dissolve it, but renders it gradually darker. The substance is free from iron. In the following the analysis is compared with Mulder's analysis of hæmatosine, from which it appears that hæmatoidine contains 1 equiv. more water than hæmatosine, but no iron:—

			Hæmatosine, $C^{44} H^{22} N^3 O^6 Fe$.
C	65·046	65·851	65·84
H	6·370	6·465	5·37
N	..	10·505	10·40
O	18·088	17·178	11·75
Ash	0·002	0·002	Fe=6·64

The numbers obtained by the author agree very closely with those found by Mulder in 1839, in the analysis of evidently pure hæmatosine. If the iron be extracted from non-crystallizable hæmatosine by digestion with sulphuric acid or by chlorine (Mulder), there remains a body which has the above composition if the iron be deducted, namely, C 70·49, H 5·76, N 11·16, O 12·59; these numbers lead to the formula $C^{14} H^8 NO^2$, instead of $C^{44} H^{22} N^3 O^6$, as supposed by Mulder in comparison with hæmatosine. The formula deduced from the author's analyses of hæmatoidine is—

$$C^{14} H^9 NO^3 = C^{14} H^8 NO^2 + HO.$$

Hæmatoidine is therefore a product of the decomposition of hæmatosine, produced by the exchange of 1 atom of iron for 1 atom of water. The quantity of hæmatoidine obtained by the author from the cyst, represents about 1800 grms. of blood, which must have been gradually effused to form this quantity.—*Comptes Rendus*, xli. p. 506.

On the Production of Nitric Acid. By M. S. DE LUCA.

Cavendish was the first to prove that nitrogen and oxygen are capable of combining directly, under the influence of the electric spark, when they are moist, and still more when they are at the same time in the presence of water and of a powerful base; they then give rise to a nitrate. This experiment, in point of fact, consists in the production of ozone, or modified oxygen, which with nitrogen causes the formation of nitric acid. M. Honzeau, by treating binoxide of barium with monohydrated sulphuric acid, obtained nascent oxygen, capable of completely oxidizing the elements of ammonia, of setting free chlorine and iodine from muriatic acid and iodide of potassium, of oxidizing silver, &c.; in fact, behaving like ozone itself.

Very recently M. Cloëz has shown by very exact experiments, that the nitrogen and oxygen of the air are capable of combining to form nitric acid and nitrates under the influence of porous bodies and alkalies, and in the absence of any nitrogenous or ammoniacal substance.

By passing moist ozonized air very slowly for three months (October, November, and December, 1855), principally during the night, over pure potassium and potash, I obtained nitrate of potash separable from the alkaline solutions by crystallization. The total volume of air employed was 7000 or 8000 litres. The air, before being ozonized, in a large flask containing phosphorus under a stratum of water, was passed over carded cotton and into an apparatus of peculiar form containing potash and sulphuric acid; it was thus freed from suspended matters and from nitrogenous substances. M. Ubaldini and myself have proved the sensibility of this ozonized air, and ascertained by means of starched paper that it could *easily* set at liberty the iodine contained in $\frac{1}{100000}$ milligrm. of iodide of potassium. These results confirm those obtained by Schönbein by another process.

Previous experiments, which I propose to repeat, proved that pure potash over which a certain quantity of air had been passed during the day and in summer did not contain any nitrates, but that in winter and during the night the air was capable of producing nitrates with the potash, and that air agitated and removed every day for several months in presence of alkalies, also produced nitrates. There are however so many difficulties and causes of error in these experiments, that I only announce them as preliminary essays.

The great importance of porous bodies in the formation of nitrates is proved by the experiments of M. Cloëz; but do these bodies act upon the alkalies by the production of ozone? And would the air, if heated beyond 212° F., or even to this temperature, produce the same effects under the influence of porous bodies in presence of alkalies? Is it a matter of indifference whether the experiments are made in summer or winter, during the day or during the night, in darkness or in the presence of light, and at a constant or variable temperature? Is ozone produced more readily in winter and during the night than in summer and during the day? These are difficult questions, which can only be solved by a long-continued investigation.—*Comptes Rendus*, Dec. 31, 1855, p. 1251.

A Brown Ink for marking Linen.

The solution for writing consists of ½ an ounce of acetate of manganese in 1½ oz. of water; the linen is prepared by saturation with a solution of 1 drm. of prussiate of potash, stiffened with 1½ drm. of gum-arabic, drying, and ironing.—*Würzb. Wochenschrift*, 1855, No. 10.

On some Acetyle and Phosphorus Compounds. By H. Ritter.

At the recommendation of Prof. Limpricht, the author has instituted the following researches:—

1. *Protochloride of Acetyle.*—The mode of preparation given by Gerhardt, by the action of 1 equiv. of oxychloride of phosphorus upon 3 equivs. of acetate of soda, always furnished anhydrous

acetic acid together with the product sought for. The author prepared it more readily from glacial acetic acid and perchloride of phosphorus. The latter was put into a retort, and small quantities of glacial acetic acid were poured over it. After each addition an effervescence of muriatic acid takes place, whilst protochloride of acetyle distils over. The residue in the retort, which also contains oxychloride of phosphorus, is distilled over, and the two fluids are separated by distillation with a thermometer immersed, which, as the difference in the boiling-points is considerable, is readily effected.

Anhydrous acetic acid also furnishes protochloride of acetyle with perchloride of phosphorus; no muriatic acid is formed. Oxychloride of phosphorus and protochloride of phosphorus have no reaction upon glacial acetic acid.

2. *Protobromide of Acetyle*, $C^4 H^3 BrO^2$.—1 equiv. of glacial acetic acid, mixed with 1 equiv. of perbromide of phosphorus, furnishes protobromide of acetyle, bromide of phosphorus, and hydrobromic acid. The protobromide of acetyle is a colourless, strongly fuming fluid, which instantly acquires a yellow colour when exposed to the air. A drop of it put upon the skin, gives the latter a very permanent odour, like that of phosphuretted hydrogen. Water rapidly decomposes it into hydrobromic acid and acetic acid. Its boiling-point is about 176° F.

3. *Oxybromide of Phosphorus*, $PBr^3 O^2$.—Gladstone has already prepared this body by the decomposition of perbromide of phosphorus in moist air; he did not however obtain it pure, as according to his description it boils between 338° and 392° F. In preparing protobromide of acetyle, the author obtained oxybromide of phosphorus, after repeated rectification, in a state of perfect purity and with a constant boiling-point. At ordinary temperatures it is a crystalline mass, consisting of large laminæ, fusing at 113° to 115° F., and contracting considerably on solidification; its boiling-point is about 383° F., and its spec. grav.=2·822. Water slowly decomposes it into hydrobromic acid and phosphoric acid. Its analysis gave,—

P	10·64	1	11·11
Br	83·33	3	83·33
O	6·03	2	5·56

Liebig's *Annalen*, cxiv. p. 208.

PATENT.

Patent granted to W. H. Balmain, *for improved Methods of recovering Oxide of Manganese after it has been used in the Manufacture of Chlorine.*

This invention relates to a new or improved process for the recovery of oxide of manganese which has been used in the manufacture of chlorine. The process is also applicable in all cases where oxide of manganese is dissolved in or acted upon by acid for that purpose, whatever the oxide of manganese may be, and to whatever purpose the chlorine may be applied, whether for the production of chloride of lime, chloride of soda, chlorate of potash, red prussiate of potash, or to bleaching, or to any other application in the arts.

The invention consists in attaining an œconomical recovery of the oxide of manganese by carrying on the process in conjunction with the manufacture of muriate or hydrochlorate of ammonia from the ammoniacal water formed in making coal-gas; and the mode of proceeding is as follows:—Into a convenient tank or pan a quantity of the ammoniacal gas-water is run, and to it is added the solution of manganese produced in the manufacture of chlorine, until a further addition of the solution causes no precipitation or thickening, or until the supernatant clear liquor does not effervesce with acid. The mixture having been allowed to stand for some hours, the clear liquor is drawn off and evaporated, for the purpose of crystallizing out the hydrochlorate of ammonia contained therein. Water is then run upon the sediment, which is agitated, and is then again allowed to stand until the sediment subsides and leaves any remaining hydrochlorate of ammonia in the supernatant clear liquor, which is drawn off and treated in the same manner as the first liquor, in order to extract the hydrochlorate of ammonia therefrom. The sediment is now removed to a bed of sand or cinders, and allowed to lose as much water as will mechanically run off by drainage. It is then placed upon a hearth or ordinary furnace-bed, and heated to redness, either by means of an open fire or by flues above and below, until it ceases to burn like tinder and has assumed a black colour; by which time it will have been converted into an oxide of manganese fit for use in the manufacture of chlorine, or for any other purpose to which it might have been applied in its original form of oxide of manganese.

When the manganese is to be used for producing chlorine, it is advisable to mix lime with the sediment before drainage, or as soon as it dries upon the hearth, and thus more or less convert it into manganate of lime, which increases its power of eliminating chlorine.

When the gas-water to be operated upon is in a town at a distance from the spot where the solution of manganese is produced, or when the recovered manganese is to be used in the manufacture of glass, the liquid chloride of manganese is boiled down, and heated in a furnace to such a temperature as will render oxide of iron insoluble; in which state it is carried to the neighbourhood where the gas-water is produced, and being redissolved in water, is mixed and treated as described in the first instance.

The oxide of manganese having been used a second time, may again be recovered a third and fourth time; and if no lime or alkali-waste has been used in neutralizing the excess of acid, it may be recovered an indefinite number of times.—Dated March 31, 1855.

THE CHEMICAL GAZETTE.

No. CCCXXI.—March 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Phloretine. *By* H. HLASIWETZ.

BY treating phloretine with solution of potash, the author has decomposed this substance into two new bodies—an acid, which he calls *phloretic acid*, and a neutral body, *phloroglucine*. The results of his investigation lead the author to adopt the formula $C^{18}H^{10}O^{5}, KO$ for the phloretate of potash, and $C^{12}H^{6}O^{6}$ for phloroglucine; so that this decomposition of phloretine proves the correctness of Liebig's formula $C^{30}H^{15}O^{10}$, for we have $C^{30}H^{15}O^{10}+KO, HO=C^{18}H^{10}O^{5}, KO+C^{12}H^{6}O^{6}$.

The author dissolves 1 *oz.* of phloretine in about 400 cub. centims. of solution of potash of spec. grav. 1·25, and boils the fluid in a silver dish until it becomes thick and forms a jelly. This gelatinous, but not fused, potash-mass is dissolved in water, and a current of carbonic acid is immediately passed through it until the excess of caustic potash is converted into carbonate. The whole is then evaporated on the water-bath until it begins to solidify. The mass, which is still very brown, is then well extracted five or six times with strong alcohol. The residue (A) is preserved.

The reddish-brown filtered tinctures are put into a stoppered vessel, and æther is added as long as any separation is observed, for which purpose about twice the volume of the alcohol employed is generally required. On the addition of æther the whole immediately becomes turbid, and divides into two strata—a thick, oily, and heavy one, which collects at the bottom of the vessel; and above this the mixture of æther and alcohol, which at first is milky. When this has become clear, it is poured away, and the æther is again obtained by distillation; by this means also a small portion of the same body that has separated is usually procured. The precipitated stratum of fluid is a very concentrated solution of the potash-salt of the new acid, phloretic acid, which dissolves readily in alcohol, but is quite insoluble in æther, and is therefore precipitated.

This solution is diluted with water; the last portions of æther and alcohol are expelled from it by boiling, and when it has acquired a syrupous consistence and become cold, it is decomposed with muriatic acid until it shows a distinct acid reaction. The fluid immediately fills with crystals, and in a little time sets into a crystalline jelly, which contains the acid mixed with a little chloride of potassium. The whole is allowed to dry upon a filter, and pressed between paper, and the acid is then separated from the chloride of potassium by extraction with strong alcohol. During the spontaneous evaporation of the alcohol, large prismatic crystals are formed, which are repeatedly recrystallized. The best plan is to recrystallize from water, in which the acid is rather less soluble than in alcohol.

The residue (A) from the extraction with alcohol contains the greatest portion of another body, which was formed at the same time, but possesses no acid properties. Although, when pure, it is readily soluble in alcohol, it forms a combination with alkaline carbonates, which resists this solvent, for only small quantities of it occur with the phloretate of potash. The principal quantity of it is obtained by decomposing the potash mass, exhausted with alcohol, with a strong acid.

For this purpose it is dissolved in water, and sulphuric acid is dropped into it until the production of a distinct acid reaction. The whole may then be evaporated to dryness on the water-bath, without separating the precipitated sulphate of potash, and the saline mass extracted with strong alcohol, or, which is better, with æther and alcohol, until it appears perfectly white. The alcoholic fluids are then again distilled off, the residue is diluted with water, the last traces of the alcohol are expelled by boiling, and it is then set to crystallize. Very soon after cooling, an abundant crystallization of a body which is still strongly coloured takes place; the most striking property of this is, that it has a very sweet taste, on which account it may for the present be called phloroglucine. The mother-liquors, when again evaporated, furnish further considerable quantities of it. These two bodies are the only products of the decomposition of phloretine.

Phloretic Acid, $C^{18}H^{10}O^{5}, HO$.—Pure phloretic acid crystallizes from water in beautiful, shining, brittle prisms, often an inch in length; they are usually grouped in a stellate form. From alcohol they are obtained of greater bulk, but the most beautiful crystals are procured from æther, in which the acid is most soluble. When the ætherial solution has become of a syrupous consistence by spontaneous evaporation, crystals of more than an inch long and nearly half an inch in thickness are formed if a large quantity of the substance be present. They are stable in the air, and have a strongly acid reaction. Their taste is rather harsh, acid, and astringent.

The aqueous solution of the acid readily decomposes the carbonates, and only gives precipitates with basic acetate of lead and the proto- and pernitrates of mercury. The two latter are crystalline.

Perchloride of iron colours it green.

When mixed with ammonia and agitated with air, it acquires a red colour. Nitrate of silver is reduced by it on the addition of a little ammonia. Solution of chloride of lime gives it a transient reddish-brown colour.

It is insoluble in cold muriatic acid; the hot solution becomes brown. Concentrated sulphuric acid dissolves it when slightly heated without colour; on further application of heat, the fluid becomes greenish-brown. Oxide of manganese produces no change of colour.

In nitric acid it dissolves immediately with a reddish-brown colour. Its aqueous solution may be boiled for a long time without perceptible change. When triturated, moistened with water, and left standing in an atmosphere of ammonia, the acid deliquesces, and becomes yellowish-red. It suffers no loss of weight either when dried at 212° F. or when fused. It fuses at 272° to 276° F., and solidifies in a crystalline form.

When heated to a higher temperature, it furnishes a penetrating vapour, burns, giving very little coal, and disappears without residue. Its analyses gave—

C	64·44	64·51	64·40	64·52	18	=	108	64·66
H	6·54	6·34	6·50	6·68	11		11	6·58
O	29·02	29·15	29·10	28·80	6		48	28·76

Phloretate of Potash, KO, $C^{18} H^{10} O^5$, is obtained from carbonate of potash and the aqueous solution of phloretic acid, or by mixing a solution of phloretic acid with one of potash, saturating with carbonic acid, evaporating, and extracting the dry mass with strong alcohol. An excess of alkali causes the solution to assume a brown colour when exposed to the air.

When the alcoholic solution is allowed to evaporate spontaneously, the salt crystallizes in a radiate form, or, if the quantity be large, in prismatic laminæ, which often acquire a considerable size. It is separated from the thick mother-liquor by pressure between paper, and repeatedly crystallized. It is colourless, has a hot saline taste, effloresces in the air, and when dried at 212° F. loses the whole of its water of crystallization:—

C	52·36	18	=	108	52·68
H	4·91	10		10	4·87
O	19·99	5		40	19·53
KO	22·74	1		47	22·92

Phloretate of Soda, NaO, $C^{18} H^{10} O^5$, is prepared in the same way as the preceding. It crystallizes from the very concentrated solution, which readily acquires a reddish colour when exposed to the air, in radiate prisms, which effloresce in the air. Analysis when dried at 212° F.:—

C	..	18	=	108	
H	..	10		10	
O	..	5		40	
NaO	16·15	1		31	16·40

Phloretate of Magnesia, prepared from carbonate of magnesia and solution of phloretic acid. It forms colourless aggregated crystals, like those of wavellite.

Phloretate of Baryta, BaO, $C^{18} H^{10} O^5$, prepared by adding carbonate of baryta to a hot solution of the acid until the cessation of effervescence. It crystallizes in very beautiful, long, transparent, flat prisms. At 212° F. they become opake. Analysis:—

C	46·08	18 =	108	46·03
H	4·14	10	10	4·26
O	..	5	40	17·06
BaO	32·37	1	76·6	32·65

Phloretate of Zinc, $ZnO, C^{18}H^{10}O^{5}$, was prepared in the same way as the baryta-salt. The solution however must be filtered whilst boiling, as the salt is very difficult of solution, and falls immediately from the hot solution in beautiful, shining, flat prisms and laminæ, which increase during evaporation. Next to the baryta-salt it is the most beautiful of the salts examined; the satin-like laminæ have nearly the appearance of cholesterine. It is stable in the air. Analysis:—

C	54·47	18 =	108	54·40
H	5·04	10	10	5·03
O	..	5	40	
ZnO	..	1	40·5	

Phloretate of Silver, $AgO, C^{18}H^{10}O^{5}$.—This is easily obtained by precipitating a pure solution of the soda-salt with nitrate of silver. The fluid sets into a crystalline jelly of dazzling white needles, which must be immediately filtered without access of air, and washed with cold water. When pressed between paper, they may be air-dried in the dark, and may be afterwards further deprived of water at 212° F. The salt is very sensitive to light, and consequently, notwithstanding all the care that can be taken, is usually a little coloured. The salt also acquires colour when put whilst still damp upon the water-bath. It is readily soluble in acetic acid and ammonia. Analysis:—

C	38·67	18 =	108	39·41
H	3·82	10	10	3·65
O	..	5	40	14·61
AgO	42·68	1	116	42·33

Phloretates of Mercury.—These are produced at once by mixing the solution of the acid with protonitrate or neutral pernitrate of mercury. They are crystalline precipitates. That produced with the protosalt forms prismatic needles, and that derived from the persalt gives transparent tabular crystals.

Phloroglucine.—This body presents a great resemblance to orcine, but is distinct from that body. Like orcine, it can only be obtained in a colourless state with difficulty. The crystals first obtained by the process described at the commencement are always strongly coloured. After many experiments, the best mode of purifying them was found to consist in mixing their aqueous solution with a little solution of acetate of lead (which produces no precipitate), and immediately passing sulphuretted hydrogen through the fluid. The precipitated sulphuret of lead very rapidly removes the colour to a certain degree, the fluid becomes of a light wine-yellow colour, and, after it has been again evaporated, furnishes the body in crystals, which, especially when the process is several times repeated, possess only a yellowish tinge. They have the peculiar property of completely attracting to themselves the colouring matter of an aqueous solution, so that in proportion as they crystallize from it the solution constantly becomes more colourless.

This is however less the case with an æthereal solution. If the substance, deprived as much as possible of its colour, be allowed to crystallize from æther, in which it readily dissolves even in the cold, and the mother-liquor be quickly poured away, the crystals are nearly colourless, and the mother-liquor remains coloured; they can now be once more recrystallized from water, when they appear quite colourless. They are crystals of the rhombic system, which by slow evaporation may be made to attain the size of a lentil, and generally exhibit irregularly developed prismatic faces; they are hard, grate between the teeth, and taste much sweeter than sugar.

Their solutions produce no alterations in vegetable colours. The body crystallizes very quickly from concentrated aqueous solutions, more slowly from alcohol and æther. It is most soluble in the latter. The crystals obtained from absolute æther are anhydrous, those from aqueous solutions contain water of crystallization.

The aqueous solution behaves in the following manner with reagents:—

With the exception of basic acetate of lead, it is not precipitated by metallic salts. It reduces protonitrate of mercury, and also nitrate of silver when heated; this takes place very rapidly on the addition of a little ammonia. Perchloride of iron produces an intense violet-red colour, which is almost the same as that of phloridzine. Solution of chloride of lime gives a reddish-yellow colour, which however almost immediately disappears on the addition of a little more of the reagent. Trommer's sugar reaction is readily obtained with a solution of phloroglucine. If a solution of the body in carbonate of potash be evaporated nearly to dryness, only a trace of it is extracted by alcohol or æther; the quantity is less in proportion to the absence of water in the solvent. The ammoniacal solution of phloroglucine becomes reddish-brown when agitated with air; it afterwards becomes quite opake.

The crystals, moistened with water, deliquesce in an atmosphere of ammonia, forming a reddish-brown fluid. Nitric acid dissolves the crystals with a brown colour. Hot muriatic acid acquires a reddish-yellow colour; when cold it has no action.

From this it appears that most of the reactions of phloroglucine are exactly like those of orcine. It is distinguished from this body however by its not fusing below 212° F., and by its being stable in the air; that is to say, its colour does not change by lying in the air, as is the case with orcine. The hydrated crystals of phloroglucine effloresce when heated, but retain their form, so that they may be dried at 212° F. without alteration. When heated only a few degrees further, they become a little discoloured, but only fuse at about 428° F. When heated above this temperature a portion of them sublimes. The fused mass solidifies in a crystalline form. The odour of over-heated phloroglucine has nothing remarkable about it. Its coal burns without residue. The analyses were made with air-dried substance (A), and with substance dried at 212° to 226° F. (B):—

A.	C	44·44	44·59	44·34	B.	C	56·37	57·32	56·92
	H	6·11	6·57	6·46		H	5·08	5·05	4·98
	O	49·45	48·84	49·20		O	38·55	37·63	38·10

The air-dried substance lost 22·32 per cent. of water by drying at 212° to 226° F.; under the air-pump, 21·7 and 21·9 per cent., and after drying for twelve hours at 194° F., 22·22 per cent. From this we may calculate for A and B—

	Calculated.		Found (average).		Calculated.		Found (average).
C^{12}	12	44·44	44·45	C^{12}	72	57·13	57·00
H^{10}	10	6·17	6·29	H^{6}	6	4·76	5·08
O^{10}	80	49·38	49·26	O^{6}	48	38·11	37·92

Bromophloroglucine, $C^{12}(H^3 Br^3)O^6$.—When bromine is dropped into a tolerably concentrated solution of phloroglucine, it disappears rapidly on shaking, and causes an abundant separation of small prismatic crystals, whilst the fluid becomes a little heated. If the addition of bromine be continued until the last portions of it no longer disappear, the fluid is at last converted into a crystalline jelly of this new body, which is put upon a filter to allow the reddish-brown mother-liquor, containing hydrobromic acid, to drain from it; it is then washed with a little cold water. During the whole operation the strong odour, provocative of tears, observed also by Stenhouse in the preparation of bromorceide, is perceived. The description given by Stenhouse of the preparation of the latter body applies almost exactly to that of bromophloroglucine. The latter however behaves towards water differently from bromorceide. Thus bromorceide is said to be almost equally insoluble in hot and cold water, although it fuses in hot water and crystallizes on cooling, whilst bromophloroglucine, although difficult of solution in cold water, dissolves completely in large quantities in hot water, and on cooling shoots out of this fluid in most beautiful acicular crystals, which are often of great length, but which usually have a brownish tinge. By treating the hot fluid with animal charcoal, they may be decolorized, although with some loss; for it appears that the body undergoes a slight decomposition when boiled with water.

It dissolves very readily in alcohol, and crystallizes from this solution in concentrically grouped prisms. Caustic alkalies and alkaline carbonates dissolve it easily, with a brown colour. By lying in warm air, the crystals become dull and lose water. They may be entirely deprived of water at 212° F., and then readily fall to powder.

The analysis of air-dried substance (A), and of substance dried at 212° F. (B), gave—

A.	C	17·45	17·44	12=	12	17·26	B.	C	20·22	19·85	12	19·83
	H	2·30	2·24	9	9	2·15		H	1·27	1·46	3	0·82
	Br	57·36	57·13	3	240	57·31		Br	66·07	66·08	3	66·11
	O	...	...	12	96	23·28		O	...	...	6	13·24

The direct determination of the water gave 12·90 and 12·93 per cent. These bromine compounds allow of the adoption of no other formula for phloroglucine than the above with C^{12}. According to this we have—

$$C^{12}H^{6}O^{6}=\text{anhydrous phloroglucine.}$$

$$C^{12}H^{6}O^{6}+4HO=\text{hydrated phloroglucine.}$$

$$C^{12}\left\{\begin{matrix}H^{3}\\ Br^{3}\end{matrix}\right\}O^{6}=\text{anhydrous bromine compound.}$$

$$C^{12}\left\{\begin{matrix}H^{3}\\ Br^{3}\end{matrix}\right\}O^{6}+6HO=\text{hydrated bromine compound.}$$

Phloroglucine and Oxide of Lead, $C^{12}H^{6}O^{6}+4PbO$.—Like orcine, phloroglucine is precipitated by basic acetate of lead. The solution of the glucoside is carefully mixed with basic acetate of lead, so as to avoid any excess of the latter; the white precipitate is then rapidly washed several times with distilled water, pressed between paper, and put under the air-pump. When it has been dried in that situation, it is triturated, and further dried at 212° F.

The salt is not so unstable as that obtained from orcine, and does not, like this, acquire a red colour during its washing and drying. Analysis:—

C	12·79	12 =	72	12·41
H	1·13	6	6	1·04
O	8·48	6	48	8·58
PbO	77·60	4	446	77·97

The composition $C^{12}H^{6}O^{6}+4PbO$ consequently agrees with that of the compound of orcine and oxide of lead, which has been calculated by Laurent and Gerhardt at $C^{14}H^{8}O^{4}+4PbO$.

The splitting of phloretine, $C^{30}H^{15}O^{10}$, into phloretic acid and phloroglucine, $C^{30}H^{15}O^{10}, KO\,HO=C^{18}H^{10}O^{5}KO+C^{12}H^{6}O^{6}$, has, as the author observes, a great similarity with the decomposition of a compound æther. As regards the products of decomposition themselves, however, phloroglucine certainly has the greatest resemblance to orcine, as has been repeatedly indicated above; but the formulæ as yet give us little insight into this similarity, as that of orcine is still quite empirical:—

$$\underset{\text{Phloroglucine.}}{C^{12}H^{6}O^{6}}+C^{2}H^{2}-O^{2}=\underset{\text{Orcine.}}{C^{14}H^{8}O^{4}}.$$

The other neutral bodies of the lichens, which most probably are closely allied to each other, do not as yet allow the recognition of their relations from their formulæ:—

$C^{34}H^{18}O^{6}$ = betaorcine.
$C^{24}H^{16}O^{14}$ = picroerythrine.
$C^{18}H^{8}O^{7}$ = roccellinine.
$C^{14}H^{8}O^{4}$ = orcine.
$C^{12}H^{6}O^{6}$ = phloroglucine.
$C^{8}H^{10}O^{8}$ = erythroglucine, and perhaps
$C^{6}H^{7}O^{6}$ = mannite.

The author from this has been led to think that these bodies may be alcohols. For the present it appears to him most advisable to arrange phloretine with the following bodies:—

$$\underset{\text{Betaorsellic acid.}}{C^{34}H^{16}O^{15}} = \underset{\text{Orsellinic acid.}}{C^{16}H^{8}O^{8}} + \underset{\text{Roccellinine.}}{C^{18}H^{8}O^{7}}.$$

$$\underset{\text{Evernic acid.}}{C^{34}H^{16}O^{14}} + 2HO = \underset{\text{Orsellinic acid.}}{C^{16}H^{8}O^{8}} + \underset{\text{Everninic acid.}}{C^{18}H^{10}O^{8}}.$$

$$\underset{\text{Erythric acid.}}{C^{40}H^{22}O^{20}} + 2HO = \underset{\text{Orsellinic acid.}}{C^{16}H^{8}O^{8}} + \underset{\text{Picroerythrine.}}{C^{24}H^{16}O^{14}}.$$

$$\underset{\text{Phloretine.}}{C^{30}H^{15}O^{10}} + 2HO = \underset{\text{Phloretic acid.}}{C^{18}H^{11}O^{5}} + \underset{\text{Phloroglucine.}}{C^{12}H^{6}O^{6}}.$$

Sitzungsber. der Akad. der Wiss. zu Wien, xvii. p. 382.

On the Artificial Production of Oil of Cinnamon.

By M. L. CHIOZZA.

In a former note* the author has shown that by the action of fusing potash cinnamic acid is decomposed into benzoic and acetic acids, in accordance with the equation—

$$C^{9}H^{8}O^{2} + 2(KHO) = C^{2}H^{3}KO^{2} + C^{7}H^{5}KO^{2} + H^{2}.$$

He has now reversed this reaction, and has succeeded in producing cinnamic acid or hydruret of cinnamyle in the following manner.

A mixture of acetic aldehyde and hydruret of benzoyle, saturated with muriatic acid and gently heated, acquires a deep brown colour, with the evolution of much muriatic acid, and of a great portion of the aldehyde, which thus escapes the reaction. In a few minutes the mixture becomes turbid by the separation of drops of water. If it be then distilled, unchanged hydruret of benzoyle is first collected, and then a small quantity of a less fluid liquid, which, when purified by several rectifications and washing with alkaline solutions, presents the characters of hydruret of cinnamyle. This mode of operating is not advantageous, and the author thinks it would be better to substitute sulphuric for muriatic acid, and to operate in closed vessels.

The odour of the substance thus obtained is exactly similar to that of natural oil of cinnamon. This odour becomes particularly sweet when the resinification of the substance commences. When recently prepared it is neutral to test-papers, but by exposure to the air it becomes rapidly acidified, and soon acquires colour. Prolonged exposure resinifies it completely. The analysis of the substance, its mode of formation, and its odour left no doubt as to its nature.

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* Ann. de Chim. et de Phys., xxxv. p. 701.

The author thinks that the reactions between the two hydrurets must be regarded as an ætherification similar to that experienced by most of the organic acids in presence of the alcohols and muriatic acid. The latter, probably, reacting upon one or other of the aldehydes, causes the formation of the chlorides ClC^2H^3 or ClC^7H^5, which reacting in their turn upon the aldehydes, regenerate muriatic acid and produce the hydruret of cinnamyle,—

$$ClH + C^7H^6O = ClC^7H^5 + H^2O,$$
$$Cl^7H^5 + C^2H^4O = ClH + C^9H^8O,$$

or

$$ClH + C^2H^4O = ClC^2H^3 + H^2O,$$
$$ClC^2H^3 + C^7H^6O = ClH + C^9H^8O.$$

This mode of interpretation, of course, leads to the admission of the existence of chlorides of non-oxygenated radicals, of which the hydrates would be aldehydes, and perhaps to the modification of the formulæ hitherto ascribed to these substances.—*Comptes Rendus*, February 4, 1856, p. 222.

Improved Colorimeter. By J. W. SLATER*.

Chemists who use the ordinary tube-colorimeter in analytical operations often find some difficulty in comparing two coloured solutions. Even though the tubes may be exactly of the same calibre, yet the eye is annoyed by the refraction of light in passing through a body with curvilinear surface. The following simple arrangement, which displays the liquids between two plane surfaces, will, I think, give perfect satisfaction. From a stout glass tube, about 1½ inch in diameter, a number of portions or hoops are cut about two-thirds of an inch in width. All these are carefully ground smooth at one edge, and then cemented down upon a strip of clear plate glass. When the cement is perfectly hard, the upper edges of the glass rings are ground upon a polishing wheel so that they form a series of cells exactly equal in depth. All that is requisite, in using this colorimeter, is to fill the cells with the respective solutions to be compared, and place the apparatus upon a sheet of white paper, or, covering the whole with another slip of plate glass, equal in size to the one upon which the rings are cemented, to hold up the entire apparatus to the light. The upper plate fitting closely upon the ground edges of the rings, prevents the solutions from escaping. In this manner shades of colour may be distinguished, which, if enclosed in tubes, might be confounded even by the most practised observer.

Northern Analytical College, Sheffield,
Dec. 24, 1855.

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* Communicated by the Author.

Note on the Identity of Nitrohæmatic and Picramic Acids.

By A. GIRARD.

In a former paper the author showed that by the reducing action of sulphuretted hydrogen upon picric acid, a red, readily crystallizable acid, capable of giving rise to well-defined salts, was produced. He also proposed to compare this acid with that obtained by Wöhler by the action of the protosalts of iron upon picric acid, with which he thought his acid was perfectly identical; and this opinion has since been put forward by Gerhardt, who considers nitrohæmatic acid to be impure picramic acid. Mr. Pugh has recently published a paper to prove this identity, but the processes adopted by him are not calculated to inspire absolute confidence. He has, in fact, operated exactly as was done by Wöhler before the author had indicated the formation of picramic acid by the action of sulphuretted hydrogen. He mixes picric acid with protosulphate of iron, boils it with an excess of baryta, precipitates the soluble baryta-salt by ammoniacal acetate of lead, and *finally decomposes the lead-salt by sulphuretted hydrogen.* It is evident, in this case, that even if the protoxide of iron had not converted the picric acid into picramic acid, the sulphuretted hydrogen of itself would be sufficient to effect this reduction.

The following is the author's process to avoid the employment of sulphuretted hydrogen. When solutions of picric acid and protosulphate of iron are boiled together, no change is produced; but as soon as the precipitation of the protoxide is effected by the addition of an alkali, the liquid acquires a strong red colour, and an abundant precipitate of peroxide of iron is obtained. When the ammoniacal liquid is separated by filtration and slightly concentrated, the addition of acetic acid is sufficient to produce, almost immediately, fine red crystals presenting all the characters of picramic acid both in their forms and reactions. To confirm this analogy, the author made an analysis which gave—

	Found.	Calculated (picramic acid).
C	36·0	36·1
H	2·7	2·5

The silver-salt gave—

	Found.	Calculated.
Oxide of silver	37·3	37·6
Acid	62·7	62·4

Protosulphate of iron, therefore, like sulphuretted hydrogen, reduces picric acid to the state of picramic acid. The author has also tried Béchamp's process of reduction with protacetate of iron, and obtained the same results.

Picramic acid [$C^{12}H^{5}O^{2}(NO^{4})^{2}N$] is derived from picric acid [$C^{12}H^{3}O^{2}(NO^{4})^{3}$] by the destruction of 1 equiv. of hyponitrous acid, accompanied by the fixation of 2 equivs. of hydrogen. The author has tried whether it was possible, by the employment of other energetic reducing agents, to modify picric acid still more deeply, and break up the other equivalents of hyponitrous acid, but hitherto without result. Picramic acid only is obtained by means of the alkaline sulphurets, nascent hydrogen, the protochlorides of tin, copper, &c. The reaction of the two latter agents only takes place after they have been precipitated by ammonia. Of course, to render these results certain, the employment of sulphuretted hydrogen must be avoided.—*Comptes Rendus*, Jan. 14, 1856, p. 59.

On a new Method of obtaining Silicium. By Prof. Wöhler.

In preparing aluminium by means of kryolite ($3NaFl+AlFl^3$), according to the process recently indicated by M. H. Rose, I tried the employment of Hessian crucibles instead of iron ones. I then frequently obtained globules of aluminium covered and traversed by hexagonal crystals of a black substance with a metallic lustre. By treating this aluminium with muriatic acid, this substance was easily obtained in the form of metallic spangles, very similar to graphite, but with a lead-blue tint. This was silicium in the remarkable form discovered by M. Deville.

In reflecting on the process by which silicium is reduced in this case, it appeared probable to me, that by the contact of the alkaline fluoride with the silica of the crucible, the double fluoride of silicium and sodium was formed, and that it is this compound from which the silicium is reduced by the aluminium. This idea has been perfectly confirmed, and I am now master of the process by which silicium can be obtained at pleasure in this crystalline state. All that is necessary is to fuse aluminium with an excess of the double fluoride of silicium and potassium ($3KFl+2SiFl^3$), in an ordinary crucible, at a heat about that required for the fusion of silver. When the crucible is broken on cooling, there is always, in the midst of the fused salt, a very brittle ingot, of a very crystalline texture and a dark iron colour. This appears to be that compound of silicium and aluminium already observed by M. Deville, containing in this case a very large quantity of silicium in the state of graphite. According to the length of the fusion, it contains from 75 to 80 per cent. of silicium, which is easily obtained by treating the ingot with muriatic acid.—*Comptes Rendus*, Jan. 14, 1856, p. 48.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Artificial Ultramarine. By C. Stölzel.

The method of producing ultramarine artificially has, since its discovery, been repeatedly the subject of investigation, both scientifically and technically; and the production of artificial ultramarine can now no longer be regarded as a secret. Nevertheless the scientific questions involved in the process have never been sufficiently answered. Hitherto the influence of one or the other body in the formation has been alone discussed, and the whole theory of the formation has never been established by accurate chemical formulæ. This is explained by the various processes which go on at the same time, by the easy decomposability of the ultramarine when dissolved up for analysis, and by our insufficient acquaintance with the compounds of sulphur, and of the polythionates with the alkalies.

By various investigations which I have had occasion to make in the different stages of the ultramarine manufacture, I have been repeatedly led to the question of the cause of the blue colour. By the kindness of the manufactory of this place*, I have obtained specimens not only of the finished colours, but also of the intermediate products of red and green ultramarine. I have from this been led to make accurate analyses of the different kinds of ultramarine, and to try the action of various reagents on them.

I. *Analyses of Blue and Green Ultramarine.*

a. *Qualitative Determination.*

I found in green and blue ultramarine, prepared with sulphate of soda, besides silica, alumina, soda, and sulphur, which were the chief constituents, no inconsiderable quantities of iron, lime, and chlorine, with traces of magnesia, potash, and phosphoric acid. It is still a matter of dispute whether the iron is essential. It comes from the materials used in the preparation, especially from the alumina and charcoal (often coal); and in almost all the analyses of ultramarine, natural or artificial, it has been found to be a never-failing constituent. All the ultramarines I have investigated contained iron, though sometimes in very small quantities. Some processes require the direct addition of copperas in the manufacture, and Elsner showed that with Gmelin's process the desired colour could only be obtained when ferruginous materials were employed. Brunner used, with the exception of wood-charcoal, materials which were free from iron; and he obtained a preparation equal to that prepared with ferruginous materials. Certain manufacturers not only put no iron in, but take care that the alumina is free from iron; and it is rather a forced assumption that a small quantity of iron, which may be accidentally present, should be essential to a good colour. With the investigation of this question I am at present engaged.

With a view to obtain more beautiful tints, or greater resistance to acids, or a greater fineness for printing and painting, many manufacturers make special additions, either before or after the firing, besides such which must be regarded as adulterations, and which must by no means be neglected in the analysis. Instead of coal or charcoal, resin is sometimes added to the mixture, and may even occasionally be detected in the prepared colour.

In a specimen of ultramarine which I examined I found traces of fatty matter, which appeared to have had nitre mixed with it.

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* Kaiserslautern in Rhenish Bavaria.

b. *Quantitative Analysis.*

1. *Blue Ultramarine.*—The determination of the individual constituents was made in several portions. The first portion was used for the determination of the silica, sulphuric acid, alumina, oxide of iron, lime, and soda. Its solution in hydrochloric acid was attended with the development of sulphuretted hydrogen, and the separation of sulphur and silica. After separating the latter, the analysis of the other constituents was made in the usual manner.

In a second portion the iron was determined. As its quantity is very small in comparison with that of the alumina, the usual modes of separation cannot be employed. The quantity of iron in the mixed precipitates of iron and alumina was therefore determined by means of permanganate of potash.

A third portion was used to determine the sulphur, which is not in the form of sulphuric acid. A portion was drenched with hot aqua regia in a capacious vessel, quickly corked, and digested till the sulphuretted hydrogen liberated was fully oxidized, and the sulphur separated had disappeared, and the separated silica had become quite gelatinous. The silica was separated, and the sulphuric acid precipitated as sulphate of baryta.

The chlorine was determined in a fourth portion by the usual methods.

The composition of blue ultramarine from this manufactory was as follows:—

Al^2O^3	31·18 p. c.		
Fe..............	0·50	(Fe^2O^3 ..	0·71)
CaO............	0·44		
Na	11·10	(NaO	14·96)
SiO^3............	38·11		
SO^3	3·54		
S	4·52		
Cl..............	0·91		
MgO, KaO, PO^5 ..	traces		
	90·30		97·08
O	9·70		2·92
	100·00		100·00

Assuming that the iron and sodium were contained in the ultramarine as such, there is a deficiency of 10 per cent.; and assuming them to be contained as oxides, there is a deficiency of 3 per cent. I made therefore special search for other substances which might have escaped detection, such as resin, fat, carbonic acid. But none of these were present. An escape of sulphuretted hydrogen in estimating the sulphur might cause an error, but many analyses of the same substance gave me constant results.

It is scarcely to be doubted that the deficit is made up by the oxygen, which may be variously combined with the sodium, iron, or sulphur; but the analysis gives no clue to the mode in which this union takes place.

Green Ultramarine.—In the same manner an analysis was made of a green ultramarine to which a prize was awarded at the Munich Industrial Exhibition. In the first firing of the ultramarine, a product more or less green is obtained, and this is only converted into blue by another firing with sulphur. If the firing be effected in pots, the interior is of a particularly beautiful green (at times also red), and these pieces can then be picked out and worked up as a green. This would find many an application if the conditions for its production were more under our command. While the various analyses of *blue* ultramarine differ materially, the analyses of *green* which I have made agree essentially with those of Elsner.

Its composition is as follows:—

	Stölzel.		Elsner.
Al^2O^3	30·11 p. c.		30·00
Fe	0·49	(Fe^2O^3.. 0·7 p. c.)	0·90 Fe^2O^3
Ca	0·45		
Na	19·09	(NaO .. 25·73 p. c.)	25·50 NaO
SiO^3..........	37·46		39·90
SO^3	0·76		0·40
S	6·08		4·60
Cl............	0·37		
MgO, KaO, PO^5	traces		
	94·81	101·66	101·30
O	5·19		
	100·00		

It would hence appear that the green ultramarine is a determinate chemical compound, while in the blue, many constituents, such as silica and alumina, vary; so that the chemical compound which causes the colour is mixed with an excess of one or the other of these constituents.

It will be seen, on comparing the analyses of green and of blue ultramarine, that in the change from green to blue, while the other constituents remain the same, the absolute quantity of sulphur and sodium decreases; at the same time the relative quantity of sulphur to sodium is increased, and there is an increase in the sulphuric acid and oxygen. An increase in this last body is essential for blue ultramarine, and all technical processes require a certain free access of air.

If the firing of ultramarine be made in pots of porous clay, the contents are never equally coloured. Two, and sometimes three and four stages, are to be distinguished, and the intermediate stages are distinctly marked. These stages, though objectionable in practice, are important for a theory of the process. Sometimes in the interior there is a red core, easily changed by air and water; then a green mass, which passes through a bluish-green to a beautiful blue; and when the heat has been too strong, this is covered by a white layer. That the addition of oxygen plays an important part in the formation of blue is seen by the fact, that when the pot is emptied the green often changes suddenly into blue. The ultramarine mass has become a complete pyrophorus by the sulphide of sodium contained in it, and burns on coming into the air with the formation of sulphurous acid. In the so-called "fine firing," which is done to convert the raw product into the commercial mass of the finest shade, the oxygen of the air is allowed to act, for the raw ultramarine mixed with sulphur is heated, and the latter burnt off at as low a temperature as possible under a slow access of air.

From a consideration of the above analysis, it is clear that part of the oxygen must be in combination with sulphur, but not as sulphuric acid. Even assuming that the whole of the sodium present is in the form of soda, which is by no means the case, there is still a deficiency of 3 per cent., which must be oxygen, and there is nothing but the sulphur with which it can be combined. When sulphide of sodium is acted upon by air, or when sulphur is heated with a sulphate, as is the case in the formation of ultramarine, some lower oxygen compound of sulphur than sulphuric acid must be formed. The presence of any such compounds has however been hitherto entirely ignored.

II. *Action of various Reagents on Ultramarine.*

As these experiments were made with ultramarine from this manufactory, it is probable that that prepared by other methods may exhibit slight deviations.

1. When ultramarine was heated to redness in a platinum crucible over a Berzelius lamp, it became lighter coloured; and when the platinum crucible, enclosed in a clay one, was heated in a charcoal fire, it became quite white. The residue, heated with hydrochloric acid, evolved no sulphuretted hydrogen, but much sulphurous acid. When ultramarine was heated in a platinum tray, in a combustion-tube closed at one end, a small deposit of sulphur was formed at first in the colder part, and afterwards a few drops of sulphuric acid were condensed there. Hence the fireproof silica exercises a decomposing action at a high temperature, and hence ultramarine cannot well be used in many processes of the porcelain manufactory.

Green ultramarine, treated similarly, passed into a dark blue colour with a tinge of green, which was so constant that it was not affected by many hours' violent firing.

2. Blue ultramarine, heated in oxygen, was changed into white. When heated with saltpetre, the colour is at first heightened; but with an increase of the saltpetre the mass is completely decolorized. This heightening of the colour is no real addition to its value as a colour, for when the mass was washed out a residue remained equal in quality and quantity to that originally employed. No colour is so deceitful in external appearance as ultramarine, and the shade of ultramarine gives no clue to its real value. By fine levigation the

shade is brought down several numbers. The practical way to estimate its value is to mix it with 8 or 10 times its weight of fine China clay, and fix, from the shade produced, its real value.

By fusing ultramarine with chlorate of potash at a low temperature, no change is produced; at a higher temperature the mass is changed into a beautiful rose colour.

When *green* ultramarine was acted on by these reagents, the result was much the same as with the blue.

3. When blue ultramarine was heated in a current of dry sulphurous acid, the colour vanished gradually, and became ultimately white.

Hydrogen passed over ultramarine gently heated, acted more rapidly. The colour became gradually paler, and sulphur and sulphuretted hydrogen were evolved in quantity. At a stronger heat the mass was changed into a gray colour, which, treated with acid, evolved sulphuretted hydrogen, and heated in the oxidizing flame of the blowpipe, passed though a beautiful green to a blue.

Green ultramarine afforded, when similarly heated, ultimate products of the same appearance, though the transition was somewhat different.

4. Strong acids attack ultramarine most energetically, and this is a great hindrance to its extended use. Potash- and soda-ley have no action even if boiled; but when fused with potash or soda, blue ultramarine passes through various stages of green or red to a red. These intermediary stages are however very evanescent. By gently heating ultramarine with small pieces of potassium, some beautiful vermilion- and purple-red colours were produced, which were also evanescent.

The results obtained may be thus expressed:—

1. Blue ultramarine, heated with exclusion of air, showed a variable degree of resistance to fire. At a high temperature blue ultramarine lost its colour, and left a mass which evolved sulphurous acid on treatment with hydrochloric acid; blue ultramarine, obtained by heating green ultramarine, remained unchanged, and evolved sulphuretted hydrogen when treated with hydrochloric acid.

2. Oxidizing and reducing agents destroyed the colours of both ultramarines at a high temperature; solid potash and soda at a lower temperature, and strong acids and chlorine in the cold.

3. Hydrogen, when passed over *blue* ultramarine heated, liberated sulphuretted hydrogen, but not with green. Both left an argillaceous gray mass, which heated in the oxidizing flame of the blowpipe, passed through a green to a blue colour.

4. Solid potash and soda, and more perceptibly potassium and sodium, changed both ultramarines, when gently heated, partially into red ultramarine.

5. Green ultramarine, when not acted upon by strong reagents, had always a tendency to pass at a high temperature into blue.

These investigations I am still continuing.—Liebig's *Annalen*, January 1856.

On the Materials for making Scorifiers.

By BURBIDGE HAMBLY, F.G.S.

[Communicated by the Author.]

The following experiments were made in the Metallurgical Laboratory of the School of Mines, Museum of Practical Geology, for the purpose of determining the best material for making scorifiers, which are required to withstand the corrosive action of melted litharge, either alone or in admixture with other metallic oxides.

The substances employed were fire-clay from Glascote near Tamworth, china clay, Ulverstone hæmatite, and fine white Australian sand. Analyses of the first two mentioned substances have been made by my friend Mr. John Spiller and myself, and the results are subjoined.

The several mixtures were reduced to a fine powder, and passed through a sieve of 35 holes to the inch, wetted, thoroughly kneaded, kept in a moist state for three to four weeks, again well kneaded until properly tempered, and subsequently formed into scorifiers by means of an iron-plug mould. The scorifiers were dried very gradually, and afterwards baked in a muffle furnace at a red heat.

To test their power of resisting the action of litharge, 500 grs. of lead were scorified in specimens of each variety, at a temperature rather higher than that employed in the cupellation of silver.

The mixtures employed varied from 1½ to 2½ lbs. in weight.

Fire Clay and Australian Sand.

	No. 1.	No. 2.	No. 3.
Fire-clay	80	50	25
Sand..........	20	50	75

No. 1. This mixture worked easily, and the scorifiers obtained from it baked very well without cracking. They were hard and close in texture, had a smooth surface, and when struck emitted a sharp ringing sound. They resisted the action of litharge very well.

No. 2. This mixture did not work so easily as the former, and the scorifiers cracked slightly at the edges in baking. They were not so close in texture as the preceding, slightly friable, and when struck gave a dull sound. The action of litharge upon this variety was very considerable and unequal.

No. 3. This mixture was very difficult to work, the scorifiers cracked at the edges in baking, were open in texture and very friable. They were unable to resist the action of litharge, and were quickly pierced with small holes.

Fire Clay and Hæmatite.

	No. 4.	No. 5.
Fire-clay	75	50
Hæmatite	25	50

No. 4. This mixture worked very easily, and came out very smooth and clean from the mould. The scorifiers baked well without cracking, were hard and close in texture, with a rather rough surface and a reddish colour; when struck, they emitted a sharp sound. At a low red heat they withstood the action of litharge very well, but when the temperature was raised they were considerably acted upon.

No. 5. The scorifiers obtained from this mixture differed very little from the last in general character; the texture was more compact, and the colour a deeper red. Their power of resisting the action of litharge was inferior, and the surface left rough and uneven.

Fire Clay and China Clay.

	No. 6.	No. 7.
Fire-clay	75	50
China clay ..	25	50

No. 6. This mixture worked easily, and came clean from the mould. The scorifiers baked without cracking, had a cream colour, a fine texture, and an extremely smooth surface; when struck, they gave a clear ringing sound. They resisted the action of litharge evenly and well.

No. 7. This mixture did not work quite so easily as the last. The scorifiers were harder and closer in texture, and somewhat more yellow in colour. They did not resist the action of litharge so well, due partly to a slight tendency to crack on reheating.

China Clay and Sand.

	No. 8.	No. 9.	No. 10.
China clay..	50	66·7	80
Sand	50	33·3	20

No. 8. This mixture was very soft, incohesive, and difficult to work. The scorifiers cracked slightly at the edges in baking, and were open in texture, soft, and friable. They were considerably acted upon by litharge, but its action was equal, the surface being left quite smooth.

No. 9. This mixture possessed more consistency and cohesion than the preceding. The scorifiers cracked less in baking, and were not so soft and friable. They did not however resist the action of litharge, owing to their tendency to crack across on reheating.

No. 10. This mixture worked much better than the two preceding. The scorifiers were closer and less friable, but cracked at the edges in baking. Their resistance to the action of litharge was greater than No. 9, and nearly equal to No. 8.

These three mixtures were difficult to form into scorifiers, owing to a tendency to cling to the mould.

Fire Clay, China Clay, and Sand.

	No. 11.	No. 12.	No. 13.
Fire-clay..	33·3	20	11·2
China clay	33·3 ...	40	44·4
Sand	33·3	40	44·4

No. 11. This mixture worked well, but the scorifiers made from it cracked slightly at the edges during baking. They had a smooth surface and a moderately close texture. In testing their power of withstanding the action of litharge, one scorifier cracked across soon after being placed in the muffle, while a second and third resisted evenly and moderately well.

No. 12. This mixture did not work so well as the preceding, being rather soft and incohesive. The scorifiers cracked slightly in baking, and were closer in texture than the last. They resisted the action of litharge very badly.

No. 13. This mixture resembled the preceding in almost every respect, but though the scorifiers were slightly harder and closer in texture, they allowed the metal to pass through almost immediately, and were quite useless.

Fire Clay, Sand, Hæmatite.

	No. 14.
Fire-clay	33·3
Sand	33·3
Hæmatite	33·3

No. 14. This mixture worked easily. The scorifiers baked very well, and resembled No. 4 and 5, but were not so close in texture. They were very unequally acted upon by litharge, even at a low temperature, and when the heat was raised the metal ran through almost immediately.

The general conclusions deduced from the foregoing experiments are,—

That the addition of silica, in the form of fine sand, to Glascote clay to the amount of 20 per cent., renders the scorifier more capable of resisting the action of litharge. It also gives hardness, smoothness, and compactness; but in proportion as that amount is exceeded, the scorifier becomes more open in texture, friable, and incapable of withstanding the action of litharge.

That the addition of hæmatite to fire-clay gives to the scorifier compactness, smoothness, and power of resisting heat, without cracking; but it does not enable it to withstand the action of litharge sufficiently well at a high temperature to render its employment advantageous for the ordinary purposes of scorification, although such a scorifier is well adapted for *roasting* where litharge is not used.

That the addition of china clay to Glascote fire-clay to the extent of 20 to 25 per cent. renders the scorifier more capable of resisting the action of litharge, while the corrosion is also more uniform; it also gives smoothness and compactness. Any larger amount of china clay renders it more liable to crack on heating.

That the use of china clay and sand alone, and in combination with fire-clay in the several proportions tried, cannot be recommended, as all the scorifiers had either a tendency to crack in the furnace, or some other quality which rendered them nearly useless.

The scorifiers in ordinary use in the laboratory are made of 1 part of burnt and 2 parts of raw Glascote clay, and are moderately good, but not quite equal to those obtained from the mixtures numbered 1 and 6. I have occasionally used scorifiers obtained direct from Freiberg in Saxony, but found them very easily acted upon by litharge. Since making the foregoing experiments, I have tried some of the scorifiers sold by Messrs. Simpson and Maule of Kennington Lane, London; and so far as my very limited experience of them enables me to give an opinion, have found them, generally, superior to any previously employed.

Analyses of the Glascote Fire Clay (dried at 212° F.).

	J. Spiller.	B. Hambly.
Silica	50·68	49·40
Alumina	32·59	32·80
Protoxide of iron*	3·17	3·48
Oxide of manganese	trace	trace
Lime	0·36	0·46
Magnesia	0·44	0·42
Potash (trace of soda)	2·32	2·24
Water (combined)	9·69	9·84
Phosphoric acid Organic matter	traces	traces
	99·25	98·64
In addition to the amount of water in combination given above, the sample contained of hygroscopic water	3·09	3·00

There was no sulphur present either in the form of sulphates or as pyrites.

Analyses of China Clay (dried at 212° F.).

	J. Spiller.	B. Hambly.
Silica	74·44	73·70
Alumina	19·04	19·68
Peroxide of iron	0·61	0·71
Oxide of manganese	trace	trace
Lime	0·45	0·50
Magnesia	0·27	0·34
Potash (trace of soda)	2·07	2·40
Water (combined)	3·71	3·77
	100·59	101·10
In addition to the combined water, the sample contained of hygroscopic water	0·81	0·78

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* Some of the iron exists in the clay as peroxide.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On crystallized Silicium and Carbon—a method of producing certain Non-volatile Simple Bodies by means of their Volatile Compounds; and on the Preparation and Properties of Fluoride of Aluminium. By H. Sainte-Claire Deville.

In the course of last year I exhibited to the Academy of Sciences some silicium crystallized in pyramids with six curved faces, closely resembling those of the diamond in form. The chemical analogies which have led to boron and silicium being placed with carbon, had induced me to think that silicium might have its diamond as well as its graphite; the crystallographic analogy would thus give the most complete support to the classification of the metalloids most generally adopted. But the measurement of crystals with curved faces being impossible, I was compelled at that period to put off the definitive solution of this problem in general chemistry.

Fresh experiments now enable me to exhibit complete crystals of silicium, susceptible of precise measurement. These crystals forming needles of 6 or 7 millims. in length, are sometimes hexagonal prisms, surmounted by a very acute pyramid with curved and unmeasurable faces, sometimes rhombohedra, arranged in a chain, and the angles at the culminating edges of which are about 69° 30′, with an uncertainty of 25′ to 30′. These observations, for which I am indebted to M. Senarmont, were made upon crystals of such tenuity, that I should never have thought of putting them on the goniometer. Subsequently, having obtained some rhombohedra a little larger, I was able to measure an angle of 69° 10′, and even its supplement, which indicates that the rhombohedron has a tendency to become complete in each of the grains forming the chain of which I have already spoken.

In its colour the rhombohedric silicium resembles the oligistic iron of Elba with all its iridizations; it scratches glass strongly, and its needles are sufficiently rigid to pierce the skin of the fingers when they are taken up by their points.

These crystals are absolutely pure, as I have been able to ascertain by several analyses, which have all given the same result; they fuse at a rather low temperature, between the fusing-points of gold and brass, and then acquire with the greatest facility the form analogous to the diamond with curved faces, which appears to be peculiar to silicium obtained by fusion. Is this form identical with, or different from, the rhombohedron just described? The physical properties may allow me to prove this when I can obtain a sufficient quantity of silicium to enable me to determine them with precision, for fused silicium does not possess cleavages.

To prepare the rhombohedric silicium, I place some aluminium in a tray, and introduce it into a porcelain tube, which is traversed by a current of hydrogen saturated with vapours of chloride of silicium. The latter is placed in a tubulated flask, which is slightly heated by carefully approaching it with a red-hot coal. The tube is brought to a bright cherry-red heat, and the operation is continued until on looking into the apparatus through the widened extremity of an adapter by which it is terminated, the thick vapours of chloride of aluminium are no longer seen. The needles of silicium are taken out of the trays, and freed from any impurities which may adhere to them by treating them successively with nitromuriatic acid, boiling hydrofluoric acid, and fused bisulphate of soda. When the operation is not complete, little globules of siliciuret of aluminium are also found, which contain 40 to 50 per cent. of silicium, corresponding with the compound $SiAl^2$.

In this operation the chloride of silicium is decomposed by the aluminium, which seizes the silicium set free, producing an actual solution. Of this, each molecule of the chloride which passes over assists the concentration; and when the metallic bath is completely saturated, the silicium, being the lightest, crystallizes at the surface, as camphor would do in an alcoholic solution.

It is clear that a similar process is applicable to the preparation of any non-volatile simple bodies capable of forming volatile compounds, decomposable by a substance which is itself capable of dissolving them; they may then be obtained crystallized. Thus boron is soluble in aluminium, and may be prepared in the same way as silicium. But I cannot yet say anything certain with regard to this substance, the obtaining of which in a state of purity is attended with unheard-of difficulties. I have not yet analysed the small crystals thus obtained by means of chloride of boron.

Carbon does not combine with aluminium; consequently when chloride of carbon* is decomposed by this metal, nothing but soot is obtained. Chloride of carbon is also decomposed by sodium, but nothing but amorphous carbon is obtained, even when the crude product of the reaction is strongly calcined. In fact, sodium does not dissolve carbon.

But if iron (and especially pig iron) which has the property of dissolving carbon be treated with the same chloride of carbon, a crystalline substance is obtained very different in its appearance from the graphite of cast iron, which is produced under totally different circumstances. The crystallized carbon forms small laminæ, which are usually irregular, but many of them are evidently hexagonal; their lustre is perfectly metallic. Many of them present parallel striæ, which diverge right and left from a straight nervure in the manner of the barbs of a feather, an arrangement which generally indicates a group of crystals. It is well known that natural graphite is also hexagonal.

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* I obtain chloride of carbon by the action of chlorine upon sulphuret of carbon at a red heat; the chloride of sulphur is separated by potash from the condensed product.

I have made analogous experiments with titanium and zirconium. The difficulty of procuring zirconium perfectly free from titanium and aluminium, and the fear of describing its properties from impure specimens, prevent me from speaking of it at present.

When fluoride of silicium is substituted for the chloride in the preparation of the rhombohedric silicium, the latter is accompanied by a transparent and strongly refractive substance crystallizing in cubes, the angle of which has been measured, and which exert no action upon polarized light. Crystals of this substance, applied in the form of geodes upon unaltered fragments of aluminium, have a most deceptive resemblance to fluor spar. These crystals are not acted upon by hydrofluoric or nitrofluoric acid, which may serve to free them from adherent silicium; they are not attacked by sulphuric acid, even when boiling, which only disengages traces of hydrofluoric acid; and they are only volatilized at a bright red heat. This new substance is fluoride of aluminium perfectly free from silicium, as is proved by a great number of analyses made by several different methods. It contains 33·3 per cent. of aluminium; theory indicates 33·2 per cent. for the fluoride of aluminium, $Al^2 Fl^3$. All these properties are contrary to those which might be assumed from analogy. Moreover, it may be prepared directly by a process, which, as it appears to me, must weaken the appearance of analogy between hydrochloric and hydrofluoric acid; thus it is sufficient to pour an excess of pure hydrofluoric acid upon calcined alumina, to dry the mixture strongly, and to place it in a tube of charcoal* or platinum, which is heated to a white heat, and traversed by a current of hydrogen, to see fluoride of aluminium sublime, and become deposited on the cold parts of the tube in crystals or cubic aggregations of several centimetres in length. Thus fluoride of aluminium is one of the most beautiful crystalline substances known in chemistry, and perhaps the least acted upon by most reagents.—*Comptes Rendus*, Jan. 14, 1856, p. 49.

On Antimonial Vermilion. By E. MATHIEU-PLESSY.

The author has invented a process which furnishes antimonial vermilion of a beautiful colour, and which is sufficiently simple to be employed in its preparation on the large scale.

Hyposulphite of soda is best prepared by the action of sulphur upon sulphite of soda; it is not usually allowed to crystallize. The sulphite of soda must be in the neutral state to avoid the action of the sulphurous acid upon the hyposulphite. The sulphite of soda is most simply and cheaply prepared in the following manner, recommended by Camille Köchlin. In the upper part of a vessel, the bottom of which is broken out, a sieve containing large crystals of carbonate of soda is fixed. Into the lower part of the vessel projects a furnace-pipe bent at right angles, which is attached to a small clay furnace. Into this furnace sulphur is thrown by little and little, and burns into sulphurous acid, which passes through the tube into the vessel, and there acts upon the carbonate of soda. The combustion of the sulphur may be regulated as occasion requires through the door of the furnace; the draught is quite sufficient, and in the course of three or four days the crystals of carbonate of soda are acted upon to a considerable depth. The very friable sulphite of soda may be readily separated from the unaltered nucleus if any remains, and the latter may then be put back into the sieve. The sulphite of soda is dissolved in water so as to produce a solution of 25° B., and this is saturated whilst hot with crystallized carbonate of soda. When effervescence no longer occurs on the addition of this salt (which is the best criterion, as litmus-paper gives no satisfactory indications), or rather when the dilute sulphite furnishes a slight effervescence of carbonic acid on the addition of muriatic acid, flowers of sulphur are added, and the mixture is heated in an earthen vessel for three hours on the water-bath, stirring, and replacing the water that evaporates. When the fluid is cool, it is filtered and diluted until it shows 25° B.

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* These new vessels will be described in an early number of the 'Annales de Chimie et de Physique.'

Perchloride of antimony is prepared by heating powdered black sulphuret of antimony with commercial muriatic acid. When the evolution of sulphuretted hydrogen begins to diminish at a gentle heat, the mixture is boiled for a few minutes. On cooling, the clear liquid is decanted. To avoid inconvenience from the sulphuretted hydrogen gas evolved during the solution of the sulphuret of antimony, it may either be passed into a solution of soda, or allowed to pass through a tube drawn out to a point at the extremity, close to which the flame of a spirit-lamp is placed; by this the sulphuretted hydrogen is burnt, even when it is mixed with much aqueous vapour. The solution of chloride of antimony obtained is diluted with water to 25° B.

When the solutions of hyposulphite of soda and chloride of antimony are thus prepared, the antimonial vermilion is prepared in the following manner:—4 litres of solution of chloride of antimony and 6 litres of water are poured into a stoneware basin, and after these 10 litres of the solution of hyposulphite of soda. The precipitate which is produced by the water is rapidly dissolved by the hyposulphite of soda in the cold. The basin is now placed in a water-bath, which is heated to boiling; in this the temperature of the mixture gradually rises. Towards 86° F. the precipitate begins to form; it is at first orange-yellow, but gradually becomes darker. The temperature is allowed to rise to 131° F., when the basin is removed from the water-bath, and the precipitate is allowed to settle, which takes place rapidly. The fluid is separated from the precipitate by decantation; the precipitate is washed first with water containing one-fifteenth of muriatic acid, and afterwards with common water, then collected on a filter and dried. In the moist state the antimonial vermilion has a shining red colour, but in drying it loses a little of its lustre. It was also produced in the cold, but the process described is more certain and furnishes a finer colour.

The author has analysed the antimonial vermilion thus prepared, and at the same time examined the amount of water in the ordinary orange-red sulphuret of antimony (precipitated by sulphuretted hydrogen). 0·668 grm. of the latter lost 0·038 grm. in weight when heated to 392° F.; 0·808 grm. of antimonial vermilion showed a loss of 0·009 grm. when heated to the same temperature. The latter might be attributed entirely to hygroscopic water, and the antimonial vermilion may therefore contain no chemically-combined water. The loss of weight which the orange-red sulphuret of antimony undergoes shows, on the contrary, that this contains water chemically combined, and this loss of weight gives it the composition SbS^3+HO. The further analysis of the antimonial vermilion was effected by treating a weighed quantity of it with nitromuriatic acid containing an excess of nitric acid. A portion of sulphur remained undissolved, which, after tartaric acid had been mixed with the fluid, and the latter had been diluted with water, was separated, dried, and weighed. The fluid contained the remainder of the sulphur in the form of sulphuric acid, which was determined by precipitation with chloride of barium. The antimony was merely determined from the loss. The result of the analysis was, that the antimonial vermilion consists of 1·1 per cent. of water, 26·7 per cent. of sulphur, and 72·2 per cent. of antimony. As the water is to be regarded as non-essential, it appears that the compound consists entirely of sulphur and antimony.—*Polytechn. Centralbl.*, 1855, p. 1451.

On the Oxyphenic Acid of Wood-Vinegar. *By* MAX. BUCHNER.

Pettenkofer found that wood-vinegar contains an acid, which from its properties might be taken for pyrogallic acid. At his instigation A. Pauli investigated this body, and found that it was distinct from pyrogallic acid. The author has continued this investigation, and found that it is identical with phenic acid, pyromoritannic acid of Wagner, and pyrocatechine of Reinsch and Zwenger.

Wood-vinegar is evaporated to the consistence of a syrup, and the residue agitated with a saturated solution of chloride of sodium, in order to separate the tarry constituents. The benzoic acid remains in the solution, and is extracted therefrom by æther, which is shaken with the solution. The ætherial stratum is drawn off, and the æther got rid of by distillation.

The residue is now further distilled, whilst a current of carbonic acid is passed through the apparatus. Various distillates are obtained. The first still contains some æther, together with acetic acid; it is nearly colourless. The second is a reddish-yellow, rather thinly-fluid oil; it contains the principal part of the required acid. The third is a brown oil, in which there is still some acid, which however does not crystallize.

The second distillate, collected until the brown oil begins to pasover, sets into a crystalline jelly, which is purified. The crude wood-vinegar contains from 0·1 to 0·2 per cent. of this acid. Its amount is determined by adding potash to the wood-vinegar, and allowing oxygen to be absorbed by the fluid. 10 milligrms. of oxyphenic acid absorb 3·7 cub. centims. of oxygen at 32° F., and with a barometric pressure of 760 millims.

The acid may also be obtained directly from the wood-vinegar without previous evaporation by agitation with æther. The mixture is then left to separate, the æther is distilled off, and the residue agitated with a saturated solution of chloride of sodium. The oil separates completely from this solution, and the acid is afterwards extracted from the solution by repeated agitation with æther. If the æther be then distilled off, a fluid remains, from which the acid separates in crystals. The acid may also be obtained from the residue by sublimation in a current of carbonic acid.

The acid thus procured crystallizes in very lustrous laminæ, belonging to the rhombic system; it fuses at 231°·8 F., and volatilizes even at its melting-point; the vapour provokes sneezing. It has exactly the reactions of oxyphenic acid. Analyses:—

	I.	II.		
C	682·6	68·39	12	65·45
H	5·91	5·96	6	5·46
O	25·47	25·65	4	29·09

The analyses are,—I., of acid fused in a porcelain tray; II., of acid sublimed and fused.

The author explains the excess of carbon and hydrogen by the adhesion of a little hydrocarbon to the acid. The lead-salt A, dried at 212° F., contained 70·08 per cent. of oxide of lead; the salt B, dried at 239° F., contained 71·76 per cent. of oxide of lead. The analyses of these salts gave—

	A.		B.			
C	22·60	22·23	22·13	22·78	12	22·78
H	1·58	1·48	1·39	1·27	4	1·27
O	5·74	6·21	4·72	5·06	2	5·06
PbO	70·08	70·08	71·76	70·89	2	70·89

The author considers it not improbable that this acid may be produced from carbolic acid during the dry distillation of wood. It always accompanies the products of the dry distillation of wood, but does not occur in coal-tar.—Liebig's *Annalen*, xcvi. p. 186.

On Rutic Acid and Quercitrine. By Dr. H. Hlasiwetz.

It appears, on comparing the statements regarding these two bodies, which occur in the memoirs of Chevreul, Bolley, Bornträger, Weiss, Rigaud, and Stein, that they are identical.

Quercitrine, according to Chevreul, Bolley, and Rigaud, is a body of a sulphur- or chrome-yellow colour, consisting of microscopic crystals belonging to the rhombic system (R.).

It is soluble in 400 parts of boiling water (Bolley), or 425 parts (Rigaud). It is nearly insoluble in cold water, dissolves in 4 to 5 parts of alcohol (Bolley), and is less soluble in æther (R.). At a high temperature it dissolves in acetic acid (R).

It dissolves very readily in dilute ammonia and solution of soda; the ammoniacal solution acquires a darker colour on exposure to air, and at last becomes dark brown (R.).

The aqueous and alcoholic solutions give a dark green colour, without precipitate, with perchloride of iron; this is still perceptible after dilution to 4000 or 5000.

Concentrated nitric acid decomposes quercitrine with a violent evolution of oxide of nitrogen and carbonic acid gases, and with formation of oxalic acid. After the completion of the action, the fluid is clear and has a reddish-brown colour (R.).

When quercitrine is mixed with a quantity of water sufficient to dissolve it, and heated to boiling, the addition of sulphuric acid soon causes the separation of a body of a much brighter yellow colour, in flakes, which, on examination, are found to consist of fine, small, interlaced needles (Rigaud's quercitrine).

Water, with the addition of a little potash or soda, dissolves quercitrine easily, with a golden-yellow colour. On the addition of an acid, it separates again in flakes, and the colour disappears (R.). The fluid filtered from the quercitrine, when evaporated after neutralization with carbonate of baryta, furnishes a sweet syrup, which possesses the properties of a sugar (R.).

During dry distillation quercitrine fuses, acquires a dark colour, and becomes for the most part decomposed. The residue is a loose coal, whilst the receiver contains a small quantity of a sublimate, accompanied by the usual products of dry distillation, such as empyreumatic oils (Rigaud, Chevreul).

Rutic acid, according to Weiss, Bornträger, Rigaud, Hlasiwetz, and Stein, forms interlaced small needles, of a sulphur-yellow tinge, when they are crystallized from water; from alcohol, crystals of a rather larger size, and of a pale sulphur-yellow colour, are obtained. This colour is proper to the substance (R. and Hlasiwetz).

In the dry state the colour is pale yellow, with a slight intermixture of green. Under the microscope the portions separated from a boiling, saturated, aqueous solution are found to consist of very fine four-sided prisms, the terminal faces of which could not be determined (Stein).

A crystalline, pale greenish powder, consisting of concentrically united prisms, which appear to be interlaced, and are furnished with very pointed terminal faces. The colour is evidently proper to it (B.). But slightly soluble in cold water; even boiling water dissolves it very sparingly; on cooling, the dissolved portion is almost entirely thrown down (R. and Hl.). Slightly, if at all, soluble in all the ordinary solvents, such as water, &c. (Stein). Very slightly soluble in cold water; more so in hot (B.); most soluble in boiling alcohol of spec. grav. 0·863 per cent. (Stein). Alcohol dissolves more of it than water; the hot saturated solution remains clear on cooling, and the substance only crystallizes on the evaporation of the alcohol.

Insoluble in æther, even when boiling (B.). Æther dissolves small quantities of this body (R. and Hl.). Slightly, if at all, soluble in æther (Stein).

Soluble in large quantity in hot acetic acid; on cooling, only a portion of the dissolved acid is thrown down, the remainder being separated when the acetic acid is evaporated (R. and Hl.). Its solubility is remarkably increased by acetic acid (Stein).

It is very easily soluble in alkaline fluids, such as potash, soda, ammonia, and lime- or baryta-water. When left standing in the air, these solutions absorb oxygen, and acquire a dark brown colour (R. and Hl., B. and Stein).

In small quantities, perchloride of iron only produces a yellowish-green colour, without a precipitate; protosulphate of iron acts in a similar manner (Stein). A solution of the substance in water is rendered intensely green by perchloride of iron (R. and Hl.).

Nitric acid communicates a yellow colour to the body in the cold; on being heated, it dissolves with a red colour and with evolution of gas. It cannot be obtained unaltered from this solution (R. and Hl.). Nitric acid colours it golden-yellow, then dark olive, and lastly reddish-brown. The evaporated fluid furnishes crystals of picric acid and oxalic acid (Stein).

When moderately concentrated mineral acids are poured over it, the body immediately acquires a citron-yellow colour, and when heated it dissolves with the same colour. Subsequently citron-yellow flakes separate, which under the microscope are found to be composed of prisms grouped in a stellate form. If the dark yellow crystals obtained by means of acids be dissolved in ammonia, and the substance be again separated by a dilute acid, it reappears with the original properties which it possessed before the treatment with acid. This acquisition of a yellow colour appears to be due to an abstraction of water (R. and Hl.).

The odour of caramel diffused by the body when heated, indicates that it is a saccharine compound (Stein). After boiling with dilute sulphuric acid, the addition of caustic soda and solution of oxide of copper produces the reaction of sugar (Stein).

When heated dry, the yellow colour is heightened, first of all acquiring an intermixture of brown. If the heat is applied to it in a test-tube, yellow vapours are evolved, and a sublimate is formed, which consists of a thickish fluid intermixed with yellowish granules (Stein).

If the temperature be raised above the melting-point, decomposition commences, the fused mass becomes brown and inflated, and there remains a voluminous coal, whilst a small quantity of volatile products distils over. The formula adopted by Rigaud is founded upon a quantitative determination of the sugar; it is $C^{36} H^{19} O^{21}$. On the other hand, Bolley's analyses of this substance cannot be reconciled with this formula. Rutic acid furnished in different analyses,—

	Bornträger.		R. and Hl.	Stein.		
C	50·34	50·27	50·15	50·94	50·92	50·66
H	5·55	5·54	5·70	5·59	5·52	5·51
O	44·11	44·19	44·15	43·46	43·54	43·81

From this Bornträger first calculated the formula $C^{12} H^8 O^8$.

(Bolley adopted the formula $C^{16} H^9 O^{10}$ for quercitrine; this may be almost as well changed to $C^{16} H^{10} O^{10}$. The proportion however of 12 : 8 is as 16 : 10·06.)

Several statements indicate that this body may be obtained with different quantities of water, upon which Bornträger has already remarked, that "the slowness with which rutic acid is deposited from its solutions may perhaps arise from the circumstance that the substance possesses a different composition in solution and in its crystalline state. Perhaps in the latter it contains 1 atom more water, which is separated from it by the action of the hot solvent, but is afterwards taken up by it again very slowly during the crystallization."

Stein found for the substance crystallized from acetic acid, C 53·68, H 4·90, O 41·41, which agrees exactly with Rigaud's numbers. The hydrated substance is therefore $=C^{36} H^{19} O^{21} + 3HO$.

	Average.			
C	50·54	36 =	216	50·23
H	5·57	22	22	5·34
O	43·89	24	192	44·43

Rochleder and the author have also investigated a lead compound, the empirical expression of which they then indicated according to the adopted formula for rutic acid. When referred to the formula of quercitrine, the per-centage found almost agrees better:—

C	28·75	36 =	216	28·93
H	3·09	20	20	2·67
O	23·54	22	176	23·60
PbO	44·62	3	334·5	44·80

$$=C^{36} H^{19} O^{21} + 3PbO + HO$$

In conclusion, the author calls attention to the similarity of certain reactions of Rigaud's quercitrine and rhamnoxanthine, a body recently described by Buchner. The two bodies possess in common their external properties, their insolubility in water, ready solubility in æther, solubility and coloration with ammonia, tastelessness, and perhaps also their behaviour when heated. The particulars regarding the coloration with sulphuric acid and with perchloride of iron, and the solubility in acetic acid, are not recorded for both the substances in question, and Buchner did not possess sufficient material for the analysis of his rhamnoxanthine. To rhamnoxanthine also applies, for the most part, the description of euxanthic or purreic acid given by Erdmann and Stenhouse, and the sublimate to which Buchner refers might perhaps be purrenone.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xvii. p. 375.

On the Preparation of Succinic Acid from Malate of Lime.

By E. J. KOHL.

In the preparation of succinic acid from malate of lime, which is obtained from the juice of the berries of the mountain ash, succinate of lime is not always obtained, but sometimes butyrate and sometimes lactate of lime, with a larger or smaller quantity of succinic acid. The author has ascertained the conditions under which a favourable result may be obtained in the formation of this acid in the fermentation of malate of lime.

1. *Preparation of the Malate of Lime.*—The malic acid is obtained from the berries at the period when they begin to turn red; at this time they furnish the largest quantity of acid. The expressed juice of the berries is evaporated to half its volume, and then perfectly clarified by straining through a pointed bag, which is best made of flannel. The dark red fluid thus obtained is heated to boiling, and nearly saturated with milk of lime, purified by straining through a sieve: the point of saturation is indicated by the dark reddish-brown colour of the fluid. If too much lime be added, the fluid appears blackish-green; but this error may be corrected by a further addition of juice, for which reason it is as well to keep some of it back. The boiling is continued until the fluid is almost of the thickness of a syrup, when the malate of lime separates in a crystalline form; this is taken out with a perforated spoon, and put into a vessel in which a stage can be fixed at a greater or less elevation, according to the quantity of the malate of lime, to allow the fluid to drain away. The salt is washed in this vessel by mixing it with water and allowing it to settle, until the fluid, which at first is reddish-brown, runs away almost limpid. This is necessary for the success of the operation, and the loss thus occasioned is of no consequence, as it only amounts to 0·67 per cent. The salt thus obtained is pressed, and the quantity of fluid still contained in it is determined, so as afterwards to calculate its dry weight. If the berries employed be too ripe, only a very small quantity is obtained, and this of indifferent quality.

2. *The Ferment.*—The best ferment was always putrid caseine, but it is not a matter of indifference at what stage of putridity the caseine is. Caseine which had been pressed into a pot and kept for one and a half to two years covered with several layers of blotting-paper, gave the best results.

3. *The Fermentation.*—The washed malate of lime is stirred up with three times its weight of cold or warm water of about 77° to 86° F., in large stone pots or tubs, and to each pound of the dry lime salt 1 oz. of caseine of the above properties, triturated with water, is added; the vessel is then placed where it will be exposed to a temperature varying day and night between 51° and 72° F. The evolution of carbonic acid very soon indicates the commencement of fermentation, which takes place slowly. If this goes on in the way required for the formation of succinic acid, an excessively disagreeable odour of rotten cheese is evolved. If this disappears at

once, we may conclude that other products are being formed; if after once disappearing it recommences, we may be certain of the formation of succinate of lime, although in this case a loss will take place, which however is often very inconsiderable.

In from eight to fourteen days, or sometimes longer, during which the mixture must always be stirred every day, the fermentation is complete, and the succinate of lime formed is deposited partly in fine needles, and partly united into crusts. When once the formation of succinate of lime is completed, the mixture remains without formation of any other products except those already mentioned, which are produced in small quantities even for years. The succinate of lime thus obtained is repeatedly washed in water, and pressed; a sample is then dried upon the water-bath, so as to determine the dry weight of the whole. If it be in crusts of too large size, they must previously be broken up. This operation stands in direct relation to the

4. *Preparation of the Succinic Acid.*—For the decomposition of the succinate of lime, 50 parts of sulphuric acid are employed to 100 parts of the salt. The crude succinate of lime is stirred up with water to form a thick paste, and the necessary quantity of hydrated sulphuric acid is added by degrees, with constant stirring, during which there is of course a great evolution of heat. When the effervescence caused by the intermixture of carbonate of lime has ceased, the paste is diluted with three or four times as much water as the expected result in succinic acid from the succinate of lime employed, which furnishes nearly one-third of its weight of acid; and the whole is digested until the completion of the decomposition, which is indicated by the formation of a homogeneous mass. The brown solution of the acid is filtered away from the sulphate of lime through a pointed bag; the sulphate of lime is freed as much as possible from adherent acid by repeated diffusion in water and filtering, and then the fluid is evaporated to dryness. If a slight excess of sulphuric acid be not already present, this addition is made, and the mixture is put into a wide-necked retort; the neck of the retort must be short, with a loosely-fitting receiver, and the body of the retort surrounded with sand to a considerable height. When the acid melts, water is first condensed in the receiver; but as the acid reaches the boiling-point, it passes over in oleaginous drops, which solidify both in the neck of the retort and in the receiver. If the acid passing over, which is to a certain extent anhydrous, comes in contact with the water previously condensed in the receiver, so great an evolution of heat is produced that the mass appears to boil; it must then be cooled. The more carefully the fire is regulated, the whiter is the product. A second receiver may be substituted as soon as the acid begins to pass over. The sublimation is continued until at a high temperature white vapours begin to appear in the retort. The carbonaceous residue may easily be removed from the retort, so that the latter may be employed again for many operations. The receiver however is generally destroyed, as the acid contained in it cannot be got out without breaking it to pieces, unless it be desired to have it

crystallized, when water may be employed. The white or yellowish acid thus obtained, broken into fragments, is heated in a suitable vessel on the water- or sand-bath, until all the sulphurous acid which is produced during distillation, as well as the adherent moisture, is entirely dispelled. If it be desired to prepare the medicinal, and not a chemically pure acid, 1 drm. of *oleum succini rectificatum* is added to every pound of the dry acid, mixed with it most intimately by trituration, and again sublimed. The product of the sublimation, or the mixture of oil and acid, is dissolved in 2 parts of boiling water, filtered, and set to crystallize. To procure chemically pure acid, the whitest is selected, and treated in the known manner.

From the preceding statements it appears that the officinal acid may also be obtained directly by the simple sublimation of the crude acid impregnated with the oil of amber.

Pure succinic acid is obtained from the crude product in crystals similar to those of sulphate of quinine. The retort is immersed in the sand not deeper than it is filled with the mixture of succinic acid with a little sulphuric acid. This must not fill more than one-fourth of the retort. As soon as the dome and the entrance of the neck of the retort are covered with beautiful dendritic crystals, which however must reach down nearly to the middle of the retort, it is allowed to cool slowly. The whole belly of the retort is then found filled with this beautiful preparation down to the solidified unsublimed portion. The retort is destroyed, as the lower portion, containing the fused crude acid, must be broken away in order to procure the crystalline acid, which, when spread upon bibulous paper, is heated to expel the sulphurous acid and moisture.

This process, according to the author's experience, is the shortest and most certain. The purification of the crude acid by repeated crystallization, and decoloration by pure animal charcoal, takes up a great deal of time and causes a considerable loss; in the first case the crystals always become covered with a somewhat resinous coat, which spoils their appearance, and can scarcely be got rid of without the employment of animal charcoal.

5. *Metamorphoses of Malate of Lime.*—It is of great importance that all sugar should be washed out of the malate of lime before it is exposed to fermentation. If the salt contain sugar, it produces first of all lactate of lime, and, according to the duration of the process, and the mode in which it is carried on, metacetonate, butyrate, and acetate of lime.

In the complete conversion of malate into succinate of lime, the only subordinate products are carbonate and acetate of lime. That an incomplete change with formation of lactic acid, and secondarily of bodies produced from this, is caused by the presence of sugar in the malate of lime, is proved by the circumstance, that when grape-sugar is added to pure malate of lime before the fermentation, the result is lactate of lime, and when the action of the ferment is continued longer, it is principally metacetonate of lime, &c. According to this, it is in the power of the experimenter to produce one or other of these bodies at pleasure. The extremely bad odour of the most putrid caseine already mentioned soon gives place to that of lactic acid when sugar is present, and is not again perceptible if the latter be in sufficient quantity. The base with which the lactic acid first combines is the ammonia produced from the caseine.

The caseine, which serves as a ferment in this process, is prepared as above described. It is frequently kneaded, until at last it forms a brownish, perfectly homogeneous mass, of not the most pleasant odour. This mass exhales considerable quantities of ammonia. If caseine in the above condition be mixed with sulphuric acid, a slight odour of butyric and acetic acids is evolved on the application of heat; whilst that of metacetonic acid is very distinctly perceptible. It is clear that these acids are combined with ammonia in the putrid caseine, as solution of potash, especially when hot, sets free a considerable quantity of ammonia. When the caseine has acquired the above properties, and the fermentation of the malate of lime has been effected under the above conditions, the desired product, succinate of lime, is obtained, together with the collateral products already mentioned. The metacetonic, butyric, and acetic acids present in the caseine, combined with ammonia, are evidently the last members of the series of lactic acid formed from sugar of milk. The decomposition of the former into butyric and acetic acids by the further action of the ferment is extremely probable; and the author proposes to investigate these matters more closely.

Quite a different result is obtained in the fermentation of malate of lime when fresh caseine is employed. This still contains sugar of milk, and the lactic acid formed from it. Half-way between the fresh and putrid caseine stands that which is employed in domestic œconomy in the manufacture of cheese. This combines the properties of both. According to the degree to which putrefaction has gone, more or less succinic acid, or of the other products, is obtained by its action upon malate of lime.—*Archiv der Pharm.*, cxxxiv. p. 257.

On Protonitrite of Cobalt and Potash. By Dr. A. Stromeyer.

When a solution of a salt of cobalt is mixed with one of nitrite of potash, a beautiful yellow precipitate is obtained. Fischer, who discovered this salt, did not analyse it. St. Evre, who also obtained it, found its composition to be $N^2O^{10}CoK$, or $KO, NO^4 + CoO, NO^4$. From the reactions of this salt, the author was led to the conclusion that this constitution was incorrect. He has repeated the analysis, and has found the formula of this salt to be

$$(Co^2O^3, 2NO^3) + 3(KO, NO^3) + 2HO.$$

Like H. Rose, the author has found that this salt may serve for the detection of cobalt and the determination of its amount, but that for this purpose certain precautions must be observed. The substance to be tested for cobalt is dissolved in so much water, that for 1 part of CoO at the utmost 300 parts of water may be present. When the dilution is greater, the precipitate is formed too slowly, and deposits itself too firmly upon the walls of the vessel. A somewhat concentrated solution of nitrite of potash is then added, together with rather more acetic acid than is necessary to redissolve the precipitate of carbonates produced by any carbonate of potash that may be contained in it. The beaker is covered with a concave glass plate, and left to stand for twelve or twenty-four hours; it is then filtered, and the precipitate washed with a solution of a potash-salt. The salt is sufficiently insoluble for this purpose in solutions of chloride of potassium and nitrate and sulphate of potash; the solutions of other salts are less suited. The author cites a series of determinations to show that cobalt may thus be determined with sufficient exactitude in the presence of many bodies.

In the presence of lead, the addition of the nitrite of potash precipitates a double salt, of the composition—

$$2(Co^2O^3, 2NO^3)+3(KO, NO^3)+3(PbO, NO^3)+4HO.$$

For the preparation of nitrite of potash, the author recommends the following process:—1 part, or more exactly 101 parts (1 atom), of nitrate of potash is melted in an iron pan, and to this 2 or rather 208 parts (2 atoms) of lead are added, constantly stirring with a rather long iron rod. The lead becomes oxidized even at a dull red heat, and soon divides into a yellow powder, although the granules still contain a nucleus of lead. The heat must therefore be raised to visible redness, when flame is usually produced; but this, with quantities of a quarter of a pound of nitrate of potash, is quite harmless. The lead is then completely oxidized. The cold mass is lixiviated with water. The solution contains a little oxide of lead, which may be almost entirely precipitated by carbonic acid. There still however remains a small quantity in solution, which may be got rid of by means of a little sulphuret of ammonium. It is then evaporated to dryness, and fused to destroy any hyposulphite of potash that may have been formed, and afterwards a concentrated solution of it is prepared. 100 grms. of nitrate of potash and 208 of lead gave 0·23 of carbonate of lead and a trace of sulphuret of lead. Nitrite of soda may be prepared in the same way.—Liebig's *Annalen*, xcvi. p. 218.

On the Preparation of Mannite. By M. Bonsall.

Good manna is dissolved in water; the resinous and gummy constituents are precipitated by basic acetate of lead, and the solution is filtered. The excess of lead is removed by sulphuric acid, the solution is evaporated and mixed with alcohol. On cooling, the mannite separates.—*Archiv der Pharm.*, cxxxiv. p. 70.

ANALYTICAL CHEMISTRY.

Method of detecting Phosphorus in Cases of Poisoning.

By E. MITSCHERLICH.

THE most sensitive means of detecting phosphorus in cases of poisoning by that substance, consists in mixing the matter to be tested for phosphorus with sulphuric acid and the necessary quantity of water, distilling the mixture in a flask, and passing the vapour through a glass gas-tube into a vertical glass cooling-tube. This cooling-tube passes through the bottom of a wide glass cylinder, which is filled with cold water, and the water is renewed by means of a funnel in such a manner that cold water is constantly passed to the bottom, whilst the warmer water escapes at the top. Beneath the lower end of the cooling-tube, which passes through the bottom of the cooler, a vessel is placed to collect the distillate.

If phosphorus be contained in the substance in the flask, vapour of phosphorus passes over into the cooling-tube with the aqueous vapour, and at the point where the vapours enter the cold part of the cooling-tube, a permanent and very distinct luminosity is observed in the dark; this continues for a long time. A luminous ring is usually perceived. From substances, especially flour, which only contain one part of phosphorus in a hundred thousand, more than 3 oz. of fluid could be distilled without any cessation of the light; this took more than half an hour. In one of the experiments, the flask with its contents was left for a fortnight open in the air, and the distillation was then repeated. The luminosity was again observed with equal distinctness. Phosphorus may therefore be detected with certainty, even after the lapse of so long a time.

If volatile bodies, which prevent the luminosity of phosphorus, such as æther, alcohol, or oil of turpentine, were present, æther and alcohol would distil over; the luminosity would therefore make its appearance later. An addition of oil of turpentine prevents the luminosity, but such an admixture would not occur in forensic investigations. Ammonia would never be injurious, as it would be retained by the sulphuric acid.

In the distillate collected in the flask placed under the cooling-tube, globules of phosphorus are found, and may readily be recognized by their properties. They occurred in the treatment of a mass which contained only one-third of a grain of phosphorus in 5 oz. of material. If a mass contain much phosphorus, the distillate also contains phosphorous acid, which may be detected by reagents, and may also be converted into phosphoric acid by means of nitric acid.

The author has convinced himself that this only occurs in the distillate when the mass submitted to distillation contains phosphorus; by the careful distillation of fluids containing phosphorous and phosphoric acids, no trace of these acids is found in the distillate. They do not consequently pass over with aqueous vapour.

In seeking for phosphoric acid in the stomach, it was found, when the experiments were made with a fresh human stomach, that this yielded no soluble phosphates when boiled with water; a stomach in which putrefaction has commenced, on the contrary, furnishes such salts, so that the phosphoric acid may be obtained in the form of phosphate of ammonia and magnesia. In the case treated by the author, this phosphoric acid was derived from the phosphorus naturally contained in the substance of the stomach, and not from the oxidation of phosphorus in the stomach, as the subject had lived for two days and a half after taking coffee poisoned with phosphorus, and in this time had drunk and vomited much.—*Journ für Prakt. Chem.*, lxvi. p. 238.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Jan. 10, 1856. (Admiral Beechey, V.P., in the Chair.)

"On the Existence of Multiple Proportion in the quantities of heat, or equivalent alteration of internal space of bodies, caused by definite changes of state as produced by Chemical Combination or otherwise." By Thomas Woods, M.D.

Gay-Lussac having shown that the combining proportions of gases and vapours are either equal in volume or some multiple of each other, and other chemists, particularly Playfair and Joule, having extended the same law to solids and liquids, it is evident that *specific volume* of its combining equivalent is characteristic of matter. But as every substance is composed of matter and space, or of particles with some distance between them, as is shown by expansion and contraction, whenever volume is altered there must be either an addition to or subtraction from the internal space of the body. This alteration of volume is evident in the case of bodies expanding or contracting by gain or loss of heat; but in chemical combination, where alteration of internal space must take place also (as shown by change of temperature, and because *specific* volume being characteristic of matter, this volume must change when the matter changes, by a substitution of a mixture of two kinds of matter for one), in chemical combination, I say, this alteration of internal space is not so plainly demonstrable. Still, in the change of temperature, we have not only an evidence, but a measure of the change of state of combining bodies. For, the phenomena of heat being produced by a *dual* force acting equally in opposite directions, one body cooling or contracting as another becomes heated or expands, it may be taken for granted that whenever heat or expansion is found in one body, the opposite change is occurring in some other. Now, regarding this proposition as true, it is intended to be proved from the combinations of oxygen that the internal space of a substance is lost and gained in multiple proportion, in the definite changes of state of bodies, such as in the condensation of vapours into liquids, and liquids into solids, and the reverse; and also in chemical combinations and decompositions; and therefore that the *space* as well as the *matter* of which volume is composed can be only added to or taken away in what is called its combining equivalent.

In order to find whether the heat of chemical combination, which is taken as equivalent to the alteration of internal space, is equally produced by the same substance uniting with others, or if not, if it is given out in multiple proportion, oxygen is made to combine with several other simple bodies, and the alteration of temperature noted.

The method of oxidizing these substances, the details of each process being given in the paper, consisted in dissolving them in some suitable menstruum,—for instance, in sulphuric acid, liquor of potass, and nitric acid. When the two former are used, water is decomposed to oxidize the dissolved body; in the last case, the nitric acid is resolved into oxygen and binoxide of nitrogen, the former of which unites with the substance to be oxidized, the latter escaping. Other combinations and decompositions at the same time take place (as detailed in the paper), and being taken into account (decompositions absorbing as much heat as is produced by the combination of the constituents), the alteration of temperature by the oxidation alone is arrived at.

In this manner eighteen different metals were oxidized, but the heat of oxidation was obtained satisfactorily only with twelve. Other experimenters (Favre and Silbermann and Andrews) have, with a different object in view, found the heat of oxidation of fourteen other substances; their conclusions are added as being from unprejudiced sources, and the result of all the experiments is brought together in a table, in order to see whether the law of multiple proportion exists. The numbers found by the different experimenters are all calculated to the same standard. The unit of heat is the amount necessary to raise the temperature of 1000 grains of water 1° Fahr., and the quantity of the metal oxidized is an equivalent of each, oxygen = 1.

To find whether the law extends to change of state when no chemical combination takes place, the amount of heat given out by the condensation of an equivalent of steam, and by the solidification of an equivalent of water, is given. The following is the table giving the thermal equivalents of the several substances, the names of the experimenters, and the ratio of proportion. It is to be remarked, that the condensation of steam being in multiple proportion with the other thermal equivalents, the expansion of all other bodies into vapour must be included; for I showed in the Philosophical Magazine for January 1852 (page 48), that all bodies expand into vapour in some multiple of their atomic volumes, and their atomic volumes being in ratio also, their expansion or gain of internal space in this definite change must be in multiple proportion.

Table showing the quantity of heat produced in 1000 grs. of water by the oxidation of an equivalent of each substance, O = 1.

Name of substance oxidised.	Units of heat.	Ratio.	Name of Experimenter.
Latent heat of ice ...	·1603	·1603	
Latent heat of steam	1·287	8 times ·1603	
Iodine..................	·8	5 times ·1603	Woods.
Chlorine..............	−1·6	....	Favre and Silbermann.
Nitrogen.............	1·6	twice ·8	Woods.
Silver	1·6	....	Woods.
Selenium	2·7	....	Favre and Silbermann.
Mercury..............	2·4	3 times ·8	Woods.
Palladium	2·42	....	Woods.
Molybdenum	3·38	4 times ·8	Woods.
Carbon	3·3		Favre and Silbermann.
Arsenic	4·8	....	Favre and Silbermann.
Antimony	4·8	....	Woods.
Copper	4·9	6 times ·8	Favre and Silbermann.
Cobalt	4·8	....	Woods.
Bismuth..............	4·82	....	Woods.
Nickel.................	6·5	8 times ·8	Woods.
Lead	6·2		Favre and Silbermann.
Hydrogen	7·8	....	Favre and Silbermann.
Tin	8·0	....	Mean of Andrews and Favre and Silbermann.
Phosphorus	8·1	10 times ·8	Favre and Silbermann.
Cadmium	8·18	....	Woods.
Iron	7·95	....	Mean of Andrews and Favre and Silbermann.
Zinc	9·6	12 times ·8	Favre and Silbermann.
Manganese...........	10·4	13 times ·8	Woods.
Barium	12·8	16 times ·8	Woods.
Aluminium...........	16·16	20 times ·8	Woods.
Sodium	17·5	22 times ·8	Favre and Silbermann.
Potassium	17·3		Favre and Silbermann.

Note.—I proved in a paper published in the Philosophical Magazine for October 1851, that "the decomposition of a compound body absorbs as much heat as the combination of the elements originally produced." I believe I was the first to prove this as a general proposition, and, by so doing, laid the foundation of almost all the thermochemical researches since carried on; for, as far as I am aware, no process which took decomposition into account was used before my paper was published.

In a paper read to the British Association at Belfast, and published in the Philosophical Magazine for November 1852, I proved that the intensity of chemical affinity might be measured by the quantity of heat produced by the combination.

As regards the first of these papers, Mr. Joule published in the Philosophical Magazine for June 1852, a memoir proving exactly the same proposition, but giving me the merit of priority in a preliminary remark. It is, however, singular that Favre and Silbermann bring forward in 1853 (Annales de Chimie et Physique, vol. xxxvii. p. 507) the very same experiments to prove the same fact, and give it as their own.

As regards the second paper. In six months after its publication, Messrs. Favre and Silbermann (Annales de Chimie et Physique, vol. xxxvii. p. 484) prove the same truth with the same experiments, using exactly the same metals, and give their memoir as producing an original idea.

I notice these coincidences here as being remarkable, and because the propositions contained in the paper referred to are the groundwork of the present experiments, and also with a view to prevent an unconscious repetition on the part of Messrs. Favre and Silbermann.

Jan. 17, 1856. (Prof. William Allen Miller, M.D., V.P., in the Chair.)

On some of the Metamorphoses of Naphthalamine. By A. W. Hofmann, Ph.D., F.R.S., &c.

The great facility with which some of the nitro-hydrocarbons can be reduced by means of iron and acetic acid—the modification of Zinin's process, lately proposed by M. Béchamp—enables us to obtain the corresponding bases in larger quantity, and to examine their derivatives more minutely.

One of the bases, for the preparation of which this process is particularly applicable, is naphthalidine, or as it is more appropriately called, naphthalamine. Mr. William H. Perkin is engaged in examining the deportment of this substance with chloride of cyanogen, and the following is a summary of the results he has at present obtained.

Fused naphthalamine, when submitted to the action of chloride of cyanogen, absorbs this gas with great avidity, and is gradually converted into a dark resinous mass. This is the hydrochlorate of a new base, which has received the name of menaphthalamine, in consequence of the analogy of its origin with that of melaniline, derived by a similar process from aniline.

Menaphthalamine is separated from the hydrochlorate by potassa, washed and repeatedly recrystallized from alcohol. It contains

$$C_{42}H_{17}N_3,$$

and is formed according to the equation

$$\underbrace{2C_{20}H_9N}_{\text{Naphthalamine.}} + \underbrace{C_2NCl}_{\text{Chloride of cyanogen.}} = \underbrace{C_{42}H_{17}N_3HCl.}_{\text{Hydrochlorate of menaphthalamine.}}$$

Mr. Perkin has verified this formula of menaphthalamine by the analysis of the hydrochlorate and of the platinum salt, which respectively contain

$$C_{42}H_{17}N_3, HCl \text{ and}$$
$$C_{42}H_{17}N_3, HCl, PtCl_2.$$

Among the various metamorphoses which menaphthalamine undergoes under the influence of agents, the deportment of this substance with cyanogen has especially engaged the attention of Mr. Perkin.

Menaphthalamine, like melaniline, absorbs two equivalents of cyanogen, and is converted into a slightly crystalline buff-coloured substance, which retains feebly basic properties.

The analysis of this body, which, from its composition, may be termed dicymenaphthalamine, has led to the formula

$$C_{46}H_{17}N_5 = C_{42}H_{17}N_3 + Cy_2.$$

Dicymenaphthalamine is insoluble in water, moderately soluble in alcohol and ether. It dissolves readily in acids. The latter solution, when precipitated by potassa, immediately after it has been made, yields unchanged dicymenaphthalamine; but if the solution be allowed to stand for a few moments, a yellow substance is precipitated, which is no longer a salt of dicymenaphthalamine.

The composition of this yellow body, which, in accordance with the terminology adopted in the aniline series, may be called menaphthoximide, is represented by the following formula—

$$C_{46}H_{15}N_3O_4,$$

and its formation is illustrated by the equation—

$$\underbrace{C_{46}H_{17}N_5}_{\text{Dicymenaphthalamine.}} + 4HO + 2HCl = \underbrace{C_{46}H_{15}N_3O_4}_{\text{Menaphthoximide.}} + 2NH_4Cl.$$

In fact, the mother-liquor of this substance contains a large amount of ammonia.

Menaphthoximide may be viewed as binoxalate of menaphthalamine *minus* 4 equivalents of water—

$$\underbrace{C_{42}H_{17}N_3HC_2O_4,\ HC_2O_4}_{\text{Binoxalate of menaphthalamine.}} - 4HO = \underbrace{C_{46}H_{15}N_3O_4}_{\text{Menaphthoximide.}};$$

and this view is corroborated by the deportment of the substance with potassa, which reproduces menaphthalamine and oxalic acid.

From the preceding experiments, it is obvious that the deportment of naphthalamine with chloride of cyanogen is perfectly analogous to that of aniline. The subsequent metamorphoses of the newly-formed compound also exhibit the same analogy.

Aniline series.		Naphthalamine series.	
Aniline......	$C_{12}H_7N$	Naphthalamine	$C_{20}H_9N$
Melaniline ..	$C_{26}H_{13}N_3$	Menaphthalamine ..	$C_{42}H_{17}N_3$
Dicymelaniline	$C_{30}H_{13}N_5$	Dicymenaphthalamine	$C_{46}H_{17}N_5$
Melanoximide	$C_{30}H_{13}N_3O_4$	Menaphthoximide ..	$C_{46}H_{17}N_3O_4$

Results of much interest are to be expected from the examination of the products formed by the action of heat on menaphthoximide. It is probable that this reaction would produce the naphthalamine term, corresponding to anilocyanic and cyanic acid.

Cyanic acid..............	C_2HNO_2
Anilocyanic acid..........	$C_{14}H_6NO_2$
Naphthocyanic acid	$C_{22}H_8NO_2$

Menaphthoximide, when heated, yields, in fact, a vapour of a most penetrating organic odour; but Mr. Perkin has not yet obtained sufficient material for a more minute examination of the body to which it belongs.

THE CHEMICAL GAZETTE.

No. CCCXXIII.—April 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some new Salts of Cadmium and the Iodides of Barium and Strontium. By HENRY CROFT, D.C.L., Professor of Chemistry, University College, Toronto*.

VON HAUER has lately taken up the examination of the double chlorides and bromides of cadmium, the existence of which was first noticed by me in 1842, in a preliminary paper read before the Chemical Society of London. The investigation being interrupted very shortly after its commencement by my removal to Toronto, had never been resumed; and in the short paper laid before the Chemical Society, the formulæ had not been fully established, with the exception of that of the sodium compound, viz. $CdCl+NaCl+3Aq$, which has since been confirmed by Von Hauer.

For the two cadmio-chlorides of potassium, the two cadmio-chlorides of ammonium, and the cadmio-bromide of potassium described by me in 1842, Von Hauer proposes the following formulæ:—

$2KCl+CdCl$.	$KCl+2CdCl+HO$.
$2NH^4Cl+CdCl$.	$NH^4Cl+2CdCl+HO$.
$2KBr+CdBr$.	$KBr+2CdBr+HO$.

Von Hauer endeavours to establish the existence of three classes of salts, which he denominates chloro-sesquicadmiates, chloro-monocadmiates, and chloro-bicadmiates, represented generally by the following formulæ: $2RCl+CdCl+xHO$; $RCl+CdCl+xHO$; and $RCl+2CdCl+xHO$; and in a second paper he states that he has succeeded in preparing a number of double salts with the chlorides of barium, strontium, calcium, magnesium, manganese, &c. &c., which seem to support this theory.

The only examples of the monocadmiates as yet described are the sodium-salt (1842) and Von Hauer's barium compound:—

$$NaCl+CdCl+3Aq.$$
$$BaCl+CdCl+4Aq.$$

In my former paper I mentioned the existence of a double iodide of cadmium and potassium, for which in an anhydrous state I proposed the formula $KI+CdI$. As this, if correct, would place the salt in the class of the iodo-monocadmiates, and as according to Von Hauer those compounds are difficult to obtain, at least with the chlorides, I have made a few experiments on the subject of the double iodides and bromides, the results of which are as follows:—

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* Communicated by the Author, having been read before the Canadian Institute, January 12, 1856.

Cadmio-iodide of Potassium.—Iodide of cadmium and iodide of potassium were mixed in atomic proportions (equal equivalents), and evaporated over sulphuric acid. The double salt being exceedingly soluble in water, separated only when the solution was reduced to a very small bulk, and the crystals formed were not very perfect. They were in the form of distorted octohedra, acquiring from the extension of certain faces a resemblance to a rhombic prism with dihedral terminations. The fact that they were octohedra was proved by measurements made by my colleague, Prof. Chapman.

1·788 grm., dried between bibulous paper, gave,—

Water	0·096	=	5·36
Sulphide of cadmium	0·338		14·70 cadmium.
Iodide of silver...........	2·275		68·74 iodine.
Sulphate of potash	0·4603		11·62 potassium.

1·771 grm., very carefully dried in bibulous paper and afterwards over sulphuric acid, gave,—

Water	0·876	=	4·94
Sulphide of cadmium	0·3520		15·46 cadmium.
Iodide of silver...........	2·2675		69·17 iodine.
Sulphate of potash	0·4183		10·60 potassium.

These numbers lead to the formulæ $KI+CdI+2HO$:—

K	11·62	10·60	1	= 488·94	10·67
Cd	14·70	15·46	1	696·77	15·21
I	68·74	69·17	2	3171·14	69·21
HO	5·36	4·94	2	225·00	4·91
	100·42	100·17		4581·85	100·00

An analysis of the anhydrous salt, made in 1842, gave the following numbers, agreeing closely with the calculation:—

	Found.	Calculated.
K	11·47	11·22
Cd	16·46	15·99
I	72·85	72·79
	100·78	100·00

Cadmio-iodide of Sodium.—Iodide of sodium was prepared by treating a solution of soda with excess of iodine, decomposing by sulphuretted hydrogen, warming, neutralizing with carbonate of soda, and crystallizing.

The crystals are as described by Mitscherlich, who gives the formula $NaI+4HO$, while Giraud found a quantity of water, which would lead to the formula $NaI+5HO$.

2·108, dried in bibulous paper, lost on heating 0·4393=20·83.

2·36, dried in bibulous paper and afterwards over sulphuric acid, lost on heating 0·46=19·49.

The formula $NaI+4HO$ requires 19·44.

Iodide of cadmium and iodide of sodium were mixed in equal equivalents, and evaporated over sulphuric acid. The double salt separated in long brilliant prisms, which deliquesce very rapidly in a moderately damp atmosphere; they appeared to be four-sided prisms, but owing to their rapid deliquescence their form could not be accurately determined.

1·0285 grm., dried in bibulous paper, gave,—

Water	0·1450	= 14·09
Sulphide of cadmium	0·1950	14·74 cadmium.
Iodide of silver............	1·2400	65·14 iodine.
Sulphate of soda	0·2218	6·98 sodium.

1·4844 grm. gave,—

Sulphate of soda	0·2783	= 6·06 sodium.

These numbers lead to the formula $NaI+CdI+6HO$:—

Na	6·98	6·06	1	= 287·20	5·95
Cd	14·74	..	1	696·77	14·43
I	65·14	..	2	3171·14	65·65
HO	14·09	..	6	675·00	13·97
	100·95			4830·11	100·00

Cadmio-iodide of Ammonium.—Iodide of ammonium, obtained by digesting iodine with hydrosulphide of ammonium, was mixed with iodide of cadmium in the proportion of equal equivalents; the solution, on evaporation over sulphuric acid to a very small bulk, gave crystals similar in appearance to those of the potassium compound, remaining unchanged in a tolerably dry atmosphere. Heated in a tube, it fuses and loses a considerable quantity of water.

1·7625 grm. gave,—

Sulphide of cadmium......	0·3685	= 16·26 cadmium.
Iodide of silver	2·3775	72·66 iodine.

These numbers lead to the formula $NH^4I+CdI+2HO$:—

NH^4	..	1	= 225·00	5·21
Cd	16·26	1	696·77	16·14
I	72·66	2	3171·14	73·44
HO	..	2	225·00	5·21
			4317·91	100·00

Cadmio-iodide of Barium.—Iodide of barium, mixed in the same proportions with iodide of cadmium, gave a mass of crystals, which deliquesced so rapidly that it was impossible to examine their form.

2·281 grms., dried in bibulous paper and weighed as quickly as possible, gave,—

Iodide of silver............	2·5405	=	59·98 iodine.
Sulphate of baryta	0·6495		16·73 barium.
Sulphide of cadmium	0·3790		12·92 cadmium.
Water as loss	..		10·37

These numbers lead to the formula $BaI+CdI+5HO$:—

Ba	16·73	1	= 854·85	16·17
Cd	12·92	1	696·77	13·18
I	59·98	2	3171·14	59·99
HO	10·37	5	562·50	10·66 (as loss).
	100·00		5285·26	100·00

Cadmio-iodide of Strontium was obtained in the same manner. It crystallizes in large clear crystals, efflorescent in very dry, but deliquescent in a moderately damp atmosphere. When heated, it easily loses iodine and absorbs carbonic acid. Owing to this circumstance, the quantity of water in the following analysis is rather too large and of the iodine too small.

1·8105 grm. gave,—

Loss on heating	0·3225	=	17·81 water.
Sulphate of strontia........	0·4225		11·11 strontium.
Sulphide of cadmium	0·2720		11·68 cadmium.
Iodide of silver............	1·9370		57·80 iodine.

These numbers lead to the formula $SrI+CdI+8HO$:—

Sr	11·11	1	= 545·60	10·27
Cd	11·68	1	696·77	13·11
I	57·80	2	3171·14	59·68
HO	17·81	8	900·00	16·94
	98·40		5313·51	100·00

Owing to the small quantity of salt in my possession, the crystals could not be obtained quite free from all admixture, and the analysis does not agree very perfectly with the calculation, but sufficiently so to establish the formula.

From these experiments we may conclude that iodide of cadmium combines with alkalic and earthy iodides in the proportion of equal equivalents; the formulæ of the new compounds just described being as follows:—

$KI+CdI+2HO.$
$NH^4I+CdI+2HO.$
$NaI + CdI + 6HO.$
$BaI + CdI + 5HO.$
$SrI + CdI + 8HO.$

In this respect they partly correspond with, and partly differ from, the zinco-iodides described by Rammelsberg in Poggendorff's 'Annalen,' vol. xliii.; the formulæ of which are as follows:—

$KI+2ZnI.$
$NH^4I+ZnI.$
$NaI+ZnI+3HO.$
$BaI+2ZnI.$

In analysing the above-mentioned cadmio-iodides, the iodine was first precipitated by nitrate of silver, the excess of silver separated by hydrochloric acid, and the cadmium precipitated by sulphuretted hydrogen, &c.

If we attempt to separate the cadmium at once as sulphide, we meet with the difficulty alluded to by Stromeyer, viz. that iodide of cadmium is decomposed very slowly by sulphuretted hydrogen.

Some experiments were made to ascertain whether this difficulty of decomposition is owing to the existence of a double salt of sulphide with iodide of cadmium, but without any favourable results.

Cadmio-bromide of Sodium.—This salt crystallizes from a mixture of equal equivalents of the two bromides in small, brilliant, six-sided plates, grouped together so as somewhat to resemble the analogous double chloride. Owing however to the small amount of bromine in my possession, the quantity of salt obtained was but little, and the crystals were not so free from an admixture of other salts as to yield a satisfactory analysis.

1·316 grm. gave,—

Loss by heating	0·1465	=	11·13 water.
Sulphide of cadmium	0·4219		24·93 cadmium.
Bromide of silver..........	1·7355		56·13 bromine.
Sulphate of soda	0·2750		6·76 sodium.

The numbers, although not agreeing very well with the calculation, seem to lead to the formula $NaBr+2CdBr+5HO$:—

Na	6·76	1 =	287·17	5·47
Cd	24·93	2	1393·54	26·58
Br	56·13	3	2998·89	57·21
HO	11·13	5	562·50	10·74
	98·95		5242·10	100·00

It will seem from this that the bromide and chloride of cadmium have a tendency to form bicadmiates and dicadmiates (sesquicadmiates of Von Hauer), while the iodide forms only monocadmiates.

In preparing the above compounds, the following observations were made on the crystallized iodides of barium and strontium.

Iodide of Barium may be prepared by digesting iodine with the sulphide of barium, or with hydrate of baryta and separation of the iodate; the solution on evaporation yields fine needles of hydriodate of baryta according to Gay-Lussac. The anhydrous salt is not deliquescent according to Gay-Lussac, but very much so according to Henry. The composition of the so-called hydriodate has not been ascertained.

The salt was prepared according to the second of the above-mentioned methods, and also by neutralizing hydriodic acid with carbonate of baryta. The solution yielded tolerably large yellowish prisms, massed together so that the form could not be determined. In a damp atmosphere they deliquesce, but in a dry one effloresce, forming a white powder.

When heated, they melt in their water of crystallization, swell up and decrepitate strongly, forming a white mass which fuses on further application of heat, and on raising the temperature still higher evolves iodine. The yellow colour of the salt is due to the mother-liquor.

1·071 lost on heating ...... 0·273 = 25·49 water.
1·803 lost on heating ...... 0·466 25·84 water.
1·803 gave sulphate of baryta 0·804 26·20 barium.

These numbers require the formula $BaI+7HO$:—

Ba	26·20	..	1 =	854·85	26·48
I	..	..	1	1585·57	49·13
HO	25·49	25·84	7	787·50	24·39
				3227·92	100·00

Iodide of Strontium was formed in the same way. It crystallizes in six-sided tables; deliquescent in a damp, efflorescent in a dry atmosphere, exhibiting when heated the same characters as the salt of barium.

1·693 lost on heating .... 0·391 = 23·09 water.
1·693 gave sulphate of strontia 0·662 18·62 strontium.

The formula seems to be $SrI+6HO$:—

Sr	18·62	1 =	545·60	19·44
I	..	1	1585·57	56·51
HO	23·09	6	675·00	24·05
			2806·17	100·00

On Catechu and its Acids. *By* Dr. C. NEUBAUER.

The author has endeavoured to prepare the tannic acid of catechu in a state of purity. He followed the process recommended by Berzelius for this purpose, in which the watery extract of catechu is treated with sulphuric acid, and also another process, in which the catechu is extracted with æther. But notwithstanding the greatest care, he never succeeded in obtaining the acid pure. He has therefore submitted catechu to a close investigation, especially with regard to catechuic acid, which was prepared not only from Bombay catechu, but also from Gambir.

1. *Bombay Catechu.*—The catechu was extracted by æther in a displacement apparatus. The æther was distilled off in a current of carbonic acid, and the residue dried *in vacuo* over sulphuric acid. This residue was extracted with water; it was gently heated on the water-bath until it was dissolved; the fluid was then filtered, and left to stand in closed vessels. In twenty-four hours crystals separated; these were obtained perfectly white by washing with water.

The reddish-brown mother-liquors from the first crystals precipitate gelatine; they consequently contain tannin. Those from the subsequent crystallizations were yellowish, but when exposed to the air for a time acquired an exactly similar colour. But when these mother-liquors were evaporated to dryness, a substance was obtained which behaved exactly like the original catechu.

The author took perfectly pure snow-white catechuic acid, which did not produce the smallest precipitate in solution of gelatine, boiled it for three hours in the air, and evaporated it to dryness. The residue was reddish-brown, and dissolved in water with a dark colour; this solution again possessed the power of precipitating solution of gelatine, as had previously been observed by Wackenroder.

From a second portion of catechu, the author prepared catechuic acid in the usual manner; extracting the substance with water, and treating it with acetate of lead, &c., as described by Berzelius. The products obtained by this process and by extraction with æther are identical. The following is the analysis of catechuic acid perfectly free from ash, prepared from Bombay catechu by means of æther. The air-dried substance gave—

C	52·62	17 =	102	52·58
H	6·09	12	12	6·18
O	41·19	10	80	41·24

At 212° F. the air-dried substance lost 14·34 per cent. When heated above this temperature, the acid becomes yellow, and at last brownish, constantly losing more and more in weight, whilst its amount of carbon increases. This is the reason of the little agreement between the results of the analyses of this substance. When the author heated the acid longer than is necessary for the expulsion of the water, or until it became yellowish, he found that the amount of carbon immediately increased remarkably. Such acid gave on analysis numbers which nearly agreed with those of the analyses of Svanberg and Zwenger, as follows:—

	Neubauer.	Svanberg.	Zwenger.
C	62·62	62·53	62·383
H	5·24	4·72	4·785
O	32·14	32·75	32·832

But if the drying be only continued until the first losses of weight approach constancy, catechuic acid loses 14·34 per cent. of water, which nearly represents 3 equivs. (calculated, 13·92). Hence the simplest expression for the acid is $C^{17}H^{9}O^{7}+3HO$.

The author then precipitated a moderately warm colourless solution of catechuic acid with basic acetate of lead. The precipitate could not be dried without change of colour; it had a brown colour. Analyses of this lead-compound gave—

C	26·26	17 =	102	26·16
H	1·97	9	9	2·30
O	14·33	7	56	14·32
PbO	57·44	2	223·14	57·22

From this the formula of the lead-compound will be $C^{17}H^{9}O^{7}+2PbO$.

The analysis of catechuic acid, prepared by means of water and treatment with solution of acetate of lead, gave—

C	61·48	17 =	102	61·08
H	5·14	9	9	5·39
O	33·38	7	56	33·53

2. *Gambir Catechu, Gutta Gambir.*—From this catechu the author has prepared the acid by means of æther (A) as above, and by the method recommended by Wackenroder (B), in which the powdered gambir is digested with three times its quantity of cold water, the brown solution filtered away, and the residue decocted repeatedly with 8 parts of water. A fine product is rapidly obtained by this method. The analysis of the substance, dried at 212° F., gave—

	A.		B.				
C	61·37	61·64	61·18	61·33	17=	102	61·08
H	5·51	5·23	5·10	5·04	9	9	5·39
O	33·12	33·13	33·72	33·63	7	56	33·53

These analyses therefore prove that the catechine prepared from Bombay and Gambir catechu by different methods is one and the same substance. The individual products, with the results of their analyses, are as follows:—

Catechuic acid.	C.	H.	O.
From Bombay catechu with æther	52·62	6·09	41·29
From Gambir with æther	52·52	6·12	41·36
Calculated, $C^{17}H^{12}O^{10}$	52·58	6·18	41·24
From Bombay catechu with æther dried at 212° F.	61·14	5·27	33·59
From the residue of Bombay catechu dried at 212° F.	61·20	5·17	33·63
From Gambir with æther dried at 212° F.	61·37	5·51	33·12
From the residue of Gambir dried at 212° F.	61·18	5·10	33·72
Calculated, $C^{17}H^{9}O^{7}$	61·08	5·39	33·53

The author then made some experiments in order to ascertain whether in the decomposition of catechuic acid with boiling dilute sulphuric acid, sugar is formed. These experiments were made with large quantities of pure catechuic acid (A), and of the tannic acid of catechu as pure as possible (B); but in no case did he obtain any sugar.

In the experiments A, 10 to 12 grms. of perfectly white catechuic acid were boiled with dilute sulphuric acid (1 part $SO^{3}HO$ and 24 parts HO), for three or four hours in an apparatus, into which whatever distilled off could flow back. The catechuic acid dissolved very readily in the dilute acid when heated; the fluid was yellow and clear, but after boiling for a short time began to grow turbid, and this turbidity gradually increased until at last a dark yellow, flocculent mass separated in considerable quantity. After boiling for three or four hours, it was allowed to cool, and the cinnamon-coloured body formed was separated by filtration. The pale yellowish filtrate was freed from sulphuric acid by carbonate of baryta, and filtered; the fluid, which still retained its slightly yellow colour, was then precipitated with acetate of lead. When the excess of lead had been precipitated by sulphuretted hydrogen, the fluid, which of course must contain any sugar that might have been formed, was evaporated to dryness on the water-bath. It furnished only a small brownish residue, which dissolved in water, producing a darker colour. This solution was again precipitated with acetate of lead, and the filtrate, freed from excess of lead, again evaporated to dryness. The residue now was colourless, and consisted of a small quantity of acetate of baryta, which contained no intermixture of sugar.

In the experiment B, with the tannic acid of catechu, he adopted a method similar to that employed by Strecker in the treatment of the tannic acids. Bombay catechu was extracted with æther, the ætherial solution agitated with water, and then evaporated to dryness. The residue was dissolved in water, and the brown mother-liquor separated by filtration from the catechuic acid, which crystallized from the solution on cooling. The solution thus obtained was allowed to stand for a long time in an open vessel; a small quantity of a brown substance separated, but no catechuic acid. After filtration the solution was precipitated by sulphuric acid, which was pretty readily effected at this degree of concentration; the precipitate produced was collected on a filter, washed several times with sulphuric acid, then strongly pressed, and afterwards boiled for several hours with dilute sulphuric acid. At first the compound formed a clear solution; but after boiling for a short time, the separation of a brown body commenced, and gradually became very considerable. In proportion as this body separated, the fluid became paler, and the boiling was continued until the solution only exhibited a slight reddish colour. After filtration, the sulphuric acid was got rid of by carbonate of baryta, the filtrate was precipitated by acetate of lead, and evaporated to dryness after the removal of the excess of lead by sulphuretted hydrogen. The residue was once more dissolved in water, and treated with acetate of lead; and in this manner, by repeated evaporation, a small residue was obtained, which only separated traces of protoxide of copper from Fehling's copper test.

The brown mass separated in the decomposition of tannic acid, had a great resemblance to that produced from catechuic acid; the author has analysed the latter when dried in the air. The analysis led to the formula $C^{17} H^{10} O^{10}$; the substance was of a pale cinnamon-brown colour, and lost at 212° F. about 3 equivs. of water, or 14·4 per cent. Analyses of the air-dried substance:—

C	53·13	53·13	53·10	17	= 102	53·13
H	5·21	5·50	5·39	10	10	5·21
O	41·66	41·37	41·51	10	80	41·66

From these experiments the author draws the following conclusions:—

1. The preparation of perfectly pure tannic acid from catechu is not possible either by precipitation with sulphuric acid or by extraction with æther, as the catechuic acid contained with it in solution is also precipitated by sulphuric acid, and considerable quantities of this acid are taken up from the catechu by æther.

2. Catechuic acid does not stand in the same relation to the tannic acid of catechu that gallic acid holds to the tannic acid of galls, but probably in an exactly opposite one.

3. The peculiar characters of the different kinds of catechu are probably due only to differences in the mode of preparation.

4. The catechuic acid contained in different kinds of catechu has the same composition, $C^{17}H^{12}O^{10}$, in which 3 equivs. are water driven off at 212° F.

5. By long drying at 212° F., catechuic acid is gradually decomposed.

6. Pure catechuic acid, when decomposed by sulphuric acid, furnishes a considerable quantity of a brown insoluble substance, but no sugar.

7. The tannic acid of catechu, similarly treated, also furnishes no sugar.

8. A pure solution of catechuic acid is precipitated by sulphuric acid, and when boiled reduces protoxide of copper from Fehling's copper test.—Liebig's *Annalen*, xcvi. p. 337.

On some Reactions of Oxalic Acid. By J. W. SLATER*.

The decomposition of certain chlorides and nitrates by oxalic acid has been lately studied. It decomposes in like manner the fluoride of calcium very readily, hydrofluoric acid being evolved as if the fluor spar were treated with strong sulphuric acid.

Oxalic acid decomposes the phosphates of iron, silver, zinc, and copper, and the arseniates of iron, silver, and copper. In all these cases the arsenic or phosphoric acid is set free, with formation of the corresponding oxalate.

It dissolves the sulphurets of iron and manganese, but not those of zinc, cadmium, uranium, cobalt, mercury, or copper. This reaction may be employed for the quantitative separation of iron and manganese from zinc and cobalt.

Oxalic acid decomposes most of the chromates, though in no case is chromic acid liberated. The chromate of zinc is first dissolved, forming a yellow solution. On standing, or more rapidly on the application of heat, the solution becomes turbid, oxalate of zinc is deposited as a white powder, whilst oxalate of chrome remains in solution. The chromates of bismuth, baryta, mercury, and lead are all immediately decomposed by oxalic acid without previous solution. The chromate of lead is scarcely affected if it has been strongly dried.

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* Communicated by the Author.

Chloride of antimony is decomposed by strong solutions of oxalic acid. The precipitate is free from chlorine. It is only very slowly decomposed by boiling water. Glass in fine powder is readily attacked by oxalic acid. Oxalate of lime and oxalates of alkali are produced, and silica is set free. Silica does not appear to dissolve in oxalic acid under any circumstances. A variety of minerals are more or less rapidly acted on by oxalic acid, yielding products that still require examination. The influence of the lichens containing oxalic acid is probably very important in effecting the disintegration and decomposition of rocks, this acid being, as we know, capable of attacking almost every class of saline compounds.

Northern Analytical College, Sheffield,
March 21, 1856.

On the Composition of the Muscles of Animals.
By MM. VALENCIENNES *and* FREMY.

As in their investigation of the eggs of animals, the authors have examined the muscular fibre of creatures of different orders. The fibres were freed as far as possible, by anatomical means, from aponeurotic fibres, nerves, blood-vessels, fat, &c.

In the analysis of the muscles of the vertebrate animals they found the principal constituent to be *creatine.* Besides this they contained inosinic acid and creatinine. Here therefore they effected nothing more than a confirmation of the researches of Chevreul and Liebig. Creatinine, however, appears to be more generally diffused in the animal kingdom than was supposed, for it occurred in the muscles of all the Vertebrata; sometimes it was met with in a free state, when it was recognizable by its alkaline reaction, and sometimes it was combined with phosphoric acid.

The body which communicates to the muscles their acid reaction is, in some cases at all events, lactic acid; but the strong acid reaction of the muscles is usually caused by the presence of acid phosphate of potash, $KO, 2HO, PO^5$. This salt is obtained by extracting the muscles with weak alcohol, and evaporating the solution to the consistence of a syrup, when the salt crystallizes.

The quantity of this salt in the muscles appears to stand in connexion with the formation of bone. It was always found in considerable quantities in those animals which possess greatly developed bones, but in very small amount in the Articulata and Mollusca. It is easy to see that this salt may be of importance in the formation of bone, as direct experiments showed that its solution converts carbonate of lime into phosphate.

This phosphate also appears to be not without influence on the production of a phosphuretted fat which is contained in the muscles. The muscles of vertebrate animals contain a considerable amount of fat, which consists of variable quantities of oleine, margarine, and stearine. Together with these neutral fats another occurs, which in its general properties is distinct from the neutral fats. It is obtained by extracting the muscles with weak alcohol, which does not dissolve the ordinary fats. If this alcoholic solution be evaporated, the residue is a sticky mass of an amber-yellow colour, which is completely soluble in water. When treated with sulphuric acid, it is decomposed in the manner of a soap; the result is sulphate of soda and an acid which is heavier than water. This acid contains phosphorus and nitrogen, and has the same composition as Fremy's oleophosphoric acid. The phosphuretted fat of the muscles is therefore the same as that of the brain, and it is diffused in the most various parts of the organism; it diminishes in quantity with age, and varies according to the species of animal.

Thus the fishes with soft white flesh, such as the Carps, Plaice, and Flounder, contain but little of it; whilst those with a compact flesh, with a distinct taste, which are generally difficult of digestion, such as the Herring, Mackerel, Trout, and especially the Salmon, contain it in considerable quantity. It is to this phosphuretted fat that these fishes are indebted for their characteristic flavour.

In the examination of the muscles of these fishes, the authors were naturally led to investigate the colouring matter of the muscles, which is so remarkable in the Salmon, the Salmon-trout, and some other species. This coloration stands in determinate relation to the reproduction, for the Salmon has red flesh throughout the year, but it becomes paler at the spawning season; and this change of colour is still more distinct in the Trouts, the flesh of which becomes perfectly white at that period.

As the fishes do not all spawn at the same time, and the females have a stronger salmon-colour and retain it longer than the males, it follows that we may obtain from the same water trouts with white or salmon-coloured flesh. From this it follows also that the Salmon-trout is not a hybrid between the Salmon and the Trout, which moreover cannot well be the case, as the Salmon spawns in July, rarely even in August, and the Trout in December.

The colouring matter of the flesh of the Salmon has already been mentioned by Davy in his 'Salmonia.' He states that the muscles of the Salmon may be deprived of their colour by æther. The authors have found that this colouring matter consists of a fat, which possesses the properties of a weak acid, and is dissolved in a neutral fat. The authors call this body

Salmonic Acid.—It is obtained from the expressed oil of the muscles of the salmon, by shaking it with alcohol containing a little ammonia. This fluid readily takes up the colouring matter, the ammonia is then neutralized by an acid, the ammoniacal salt is allowed to separate, and the colouring matter is obtained in the form of a sticky red acid, which possesses all the properties of a fatty acid. The Salmon-trout furnishes the same acid as the salmon.

It occurs in considerable quantity, mixed with oleophosphoric acid, in the spawn of the Salmon, which accounts to a certain extent for the loss of flavour in the flesh of the Salmon during the spawning season. Different species contain different quantities of salmonic acid; thus the *Salmo hamatus*, Val., contains less than the *Salmo Salmo.*

The muscles of the Crustacea appear to be more simple in their composition than those of the Mammalia (Vertebrata?); the phosphate of potash is generally deficient, but on the other hand, the oleophosphoric acid is present in as great proportion as in the muscles of fishes. Creatine and creatinine were also obtained from several species.

Muscles of the Mollusca.—With these also the authors took great care to obtain them free from all other tissues and products of secretion. They examined the fibres of Cephalopoda (*Sepiæ*) and Acephala.

The composition of these fibres is much less complex than in the Vertebrata. They contain only inconsiderable quantities of acid phosphate of potash, oleophosphoric acid, creatine, and creatinine. Instead of the latter, it is remarkable that they found taurine. They detected this body, not only by its properties, but also by its elementary analysis. Senarmont determined the crystalline form of this taurine, and found it to be identical with that of taurine from the bile. The authors obtained taurine both from the muscles of *Sepiæ* and of the oyster. This occurrence of taurine is very remarkable, and certainly proves that it is not a product peculiar to the bile.—*Journ. de Pharm. et de Chim.*, 3 sér., xxviii. p. 401.

ANALYTICAL CHEMISTRY.

On the Separation of Protoxide of Nickel from Oxide of Iron.

By P. SCHWARZENBERG.

THE author found that small quantities of protoxide of nickel in solution with much peroxide of iron, are not completely separated from the latter by carbonate of baryta, but are partially precipitated along with it, even when the carbonate of baryta has no alkaline reaction and all heating is avoided. A better method for the separation of these oxides is the process recommended by Herschel, of neutralizing the fluid with carbonate of ammonia, and precipitating the peroxide of iron by boiling.

To the fluid containing perchloride of iron and protochloride of nickel, a sufficient quantity (at least twenty times the weight of the oxide of nickel) of muriate of ammonia is added. Carbonate of ammonia is then introduced in small quantities, very diluted and in drops, towards the close of the operation, as long as the resulting iron precipitate is again dissolved, which at first takes place rapidly, but afterwards more slowly. At the right degree of saturation, which, when the solution is not too concentrated, may be easily ascertained, the fluid has lost its transparency, although no precipitate can be detected in it; and when it is left standing for some time, it does not regain its transparency, but rather becomes more opake. The solution is now gradually heated to boiling, and kept at that temperature for a short time after the expulsion of all the carbonic acid. The iron separates in the form of a basic salt, which is rapidly deposited if the solution be not too concentrated. When the addition of a drop of ammonia to the solution which has become clear shows that all the iron is precipitated, a further small quantity of ammonia is added to convert the precipitated basic iron salt into hydrated peroxide of iron; this is necessary because the basic iron salt dissolves partially in the fluid, especially on cooling. The fluid, which contains all the nickel, is filtered from the hydrated oxide of iron, and the nickel and iron determined in the usual way.

Exact results are obtained in this way when the fluid is not too concentrated (it must not contain more than 3·4 grms. of peroxide of iron in the litre), and does not contain considerable quantities of sulphuric acid. In the latter case a basic iron salt separates, even at ordinary temperatures, during the saturation with carbonate of ammonia, before a sufficient quantity of this has been added, so that the right degree of saturation cannot be exactly observed. In such a case the sulphuric acid is to be precipitated by an exactly sufficient quantity of chloride of barium, or the oxide of iron may be precipitated by ammonia, dissolved in muriatic acid, and separated from the nickel mixed with it in the manner above described.

A series of analytical experiments with fluids which contained known quantities of peroxide of iron and protoxide of nickel, in which the separation was effected both by the above process and by means of carbonate of baryta, led the author to conclude,—1st, that the complete separation of protoxide of nickel from peroxide of iron by means of carbonate of baryta, is certain of success only when the solution contains a sufficient quantity of muriate of ammonia; and 2ndly, that the above-described process with carbonate of ammonia gives better results than the method with carbonate of baryta without the addition of muriate of ammonia, and as good as those obtained in that way with a sufficient quantity of muriate of ammonia. —Liebig's *Annalen*, xcvii. p. 216.

A new Method for detecting the Presence of Sulphur in Hops.

By Dr. RUD. WAGNER.

The question, whether or not a sample of hops has been treated with sulphurous acid during the drying, is one of more than ordinary difficulty to decide.

The brewers of Bavaria pour water on a handful of the hops, and place in the mixture a silver spoon, and imagine that if the hops have been sulphured, black stains of sulphuret of silver will be produced on the spoon.

This test is a very uncertain one, and scarcely succeeds once in ten times. A comparatively very large amount of sulphurous acid is required in order to produce a stain of sulphuret on the surface of the silver, in which case it can be detected better by the smell than by any chemical test. Now when it is considered that commonly 1 lb. of sulphur is used to 2 cwts. of hops, that fully a fourth of this quantity remains unburnt, that more than half of the sulphurous acid escapes into the atmosphere owing to the method employed, it will be seen how small a proportion of sulphurous acid is efficaciously applied.

This small proportion of sulphurous acid can only be discovered by the silver-test when the hops have been sulphured a short time previous to its application (eight to fourteen days); and in this case an observable stain of sulphuret only appears when the mixture of hops and water has been left to itself at a moderate temperature for several days, when, in consequence of the fermentation which takes place, the sulphurous acid is reduced to sulphur. To an opinion recently put forth, that metallic silver was capable, in the absence of organic matter, of converting sulphurous acid into sulphuric acid and sulphur, the author can by no means assent, as he has convinced himself by experiment that metallic silver may remain in contact with a very dilute watery solution of sulphurous acid for a fortnight without the smallest stain of sulphuret appearing on its surface.

An examination with a magnifying lens, in order to ascertain from the form and colour of the lupulin whether the hops have been sulphured, is no longer possible in the present condition of the hop trade of Bavaria, where the hops are not treated with sulphur for any dishonest purpose, as seems to be the opinion in North Germany, but merely to improve their keeping qualities, and render them more fit for exportation.

The author has tried the method proposed by Dr. Heidenreich of Ansbach upwards of three years ago, and employed it in numerous instances in judicial proceedings. According to this, twenty or thirty of the cones of the hop are placed in a flask with zinc and muriatic acid, and the hydrogen evolved passed through a solution of acetate of lead; if the hops contained sulphurous acid, sulphuretted hydrogen is produced, and causes a dark brown precipitate of sulphuret of lead.

This process is satisfactory when the hops have been sulphured within a few (three to four) weeks, but is not sufficiently delicate when the object is to detect a minute trace of sulphur.

The author has effected an improvement on Heidenreich's method. It now affords us a means of detecting sulphurous acid, not only in hops, but also in all other substances, such as wines, bleached silk, &c., even when it exists in such minute quantity as to escape detection by any other method.

The test is founded on the fact, that a solution of nitroprusside of sodium is coloured a magnificent purple by the smallest trace of an alkaline sulphuret, such as sulphuret of potassium or ammonium.

In the employment of the test, a solution of nitroprusside of sodium, so dilute as to appear of a very light brown colour, is placed in a beaker, and a few drops of solution of caustic potash added. The process is now conducted as in Heidenreich's method. The hops under examination are placed in a flask with a piece of sheet zinc, diluted muriatic acid poured over them, and the gas conducted into the solution of the nitroprusside. If the gas contain but a minimum of sulphuretted hydrogen, the first bubble causes a violet cloud in the solution; after passing the gas for a short time, it assumes the magnificent colour of the solution of permanganate of potash. The vapour of muriatic acid passing over with the gas, does not affect the reaction unless it be continued too long. It will be readily understood that the gas should not be washed; at most it should be filtered through cotton-wool.

In hops which have been sulphured, it is impossible to detect the sulphur after a few months.

This test for sulphurous acid is not only one of the most delicate in the whole range of analytical chemistry, it is also one of the simplest and most beautiful.—*Kunst- und Gewerbeblatt für Bayern.*

On the Characters of Red Wines adulterated with Alum, and their Application to the Detection of small Quantities of that Salt introduced into Wine. By J. L. Lassaigne.

The author has found that the aluminous salts, when dissolved in red wines, are partially decomposed with more or less rapidity, according to the temperature at which the operation is carried on. The result of this reaction is the precipitation of a coloured compound, formed by the union of the alumina with a portion of the colouring matter of the wine; and this compound, which varies slightly in colour according to the kind of wine, is a true lake, such as is produced by alumina with most of the organic colouring principles.

When a red wine is boiled for a few minutes with a very small addition of alum, it gradually becomes turbid, and furnishes a flocculent precipitate, which collects at the bottom of the vessel when the wine is allowed to cool and stand; it forms a completely insoluble lake. This deposit, which may easily be separated by decantation and filtration, presents reactions characteristic of the colour derived from the wine itself; when calcined in contact with the air in a platinum crucible, it leaves a tolerably abundant, white, pulverulent residue, presenting all the characters of anhydrous alumina.

Pure red wines, without any addition of aluminous salt, are not rendered turbid even by long boiling; and besides, the deposit which they may sometimes furnish under these circumstances, would not present the composition above indicated. The author adds, that by this simple process, potash or ammoniacal alum may be quickly detected in wines containing $\frac{1}{1000}$, $\frac{1}{2000}$, or even $\frac{1}{3000}$ of these salts.—*Comptes Rendus*, Feb. 25, 1856, p. 410.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Employment of Sulphuret of Carbon for Industrial Purposes. By E. Deiss.

The author commences by stating, that in 1840 the price of sulphuret of carbon was as high as from 50 to 60 francs the kilogramme, but that soon afterwards he reduced its price so greatly that in 1848 he sold it at 8 francs the kilogramme for the purpose of vulcanizing india-rubber. At present, with an apparatus composed of three retorts, he is able to manufacture the immense quantity of 500 kilogrammes of sulphuret of carbon in twenty-four hours; although scarcely a year ago, with the same furnace, the same retorts, and the same amount of fuel, he could only produce 150 kilogrms. in the same time. The product now costs him only 50 centimes the kilogramme, and he has no doubt that, by operating on a larger scale, it might soon be sold at 40 francs per 100 kilogrms. As however this substance has at present only a very limited employment in the vulcanization of india-rubber, the author having a large quantity on his hands, naturally desired to find some other purpose to which it might be applied; and considers that he has discovered one of the greatest importance, namely, the extraction of fatty matters.

He states that Paris daily produces 30,000 kilogrms. of bones, which are collected by the *chiffoniers*, and carried to the manufactories of ivory-black and gelatine. Here they are sorted, some being devoted to the production of ivory-black, others of gelatine, whilst some are sold to the workers in bone. The greater part of them (25,000 kilogrms. daily) are employed in the manufacture of ivory-black; but these undergo a preliminary treatment for the extraction of their fatty matter. The bones are broken and boiled with water for about three hours in large caldrons; the fat floats on the surface and is skimmed off; the bones are taken and thrown into a heap, to undergo a kind of fermentation, in which the production of heat induces a state of desiccation which fits the bones for calcination.

In these operations the bone undergoes a great alteration: the long boiling in water dissolves a great portion of the gelatine, which is necessary for the production of a good black; and the fermentation and long exposure to the air causes the almost total destruction of the animal matter, so that a bad black is produced for the sake of only 5 or 6 per cent. of fat.

The author states that much more advantageous results may be obtained by the employment of sulphuret of carbon. He proposes to crush the bones almost to powder; then to treat them with this agent, which almost instantly dissolves all the grease contained in them; and from this it may be separated by distillation, which is greatly facilitated by the low temperature at which this fluid boils, and the ease with which it may be condensed. The quantity of grease thus obtained is 10 or 12 per cent., and it is superior to that procured by boiling.

He adds, that the same agent may be applied to the extraction of oils from oleaginous seeds and of the grease from wool. In the latter case the grease extracted becomes a useful product; it is a butyraceous substance, adapted for the manufacture of some kinds of soap.—*Comptes Rendus*, February 4, 1856, p. 207.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Feb. 21, 1856. (The Lord Wrottesley, President, in the Chair.)

"On the Bromide of Titanium." By F. B. Duppa, Esq. Communicated by A. W. Hofmann, Ph.D., F.R.S. &c.

A comparison of the boiling-points of corresponding chlorine and bromine compounds, led Prof. Kopp to the interesting discovery, that on the average their boiling-points rise 32° C for every equivalent of bromine which is substituted for an equivalent of chlorine.

	Boiling-point.	Difference.
Chloride of ethyle, $C_4 H_5 Cl$	11° C.	30.
Bromide of ethyle, $C_4 H_5 Br$	41° C.	
Dichlorinated ethylene, $C_4 H_4 Cl_2$	67° C.	$66=2\times 33$.
Dibrominated ethylene, $C_4 H_4 Br_2$	133°·6 C.	
Terchloride of phosphorus, $P Cl_3$.	78° C.	$97=3\times 32\frac{1}{3}$.
Terbromide of phosphorus, $P Br_3$.	175° C.	

If this difference be constant for all chlorine and bromine compounds, it becomes obvious that very important inferences in respect to the atomic constitution of these substances may be derived from the determination of their boiling-points. This result has, in fact, been happily applied by Prof. Kopp, as a criterion to determine the equivalent of silicium, a matter of such uncertainty as to have led to the admission of not less than three formulæ for silica—

$$SiO$$
$$SiO_2$$
$$SiO_3.$$

From the difference between the boiling-points of chloride (59° C.) and that of bromide (153° C.)—a difference which amounts to $94=3\times 31\frac{1}{3}$—Kopp derives the formulæ

$$SiCl_3 \text{ and } SiBr_3,$$

as representing the atomic constitution of the chloride and the bromide of silicium, and he accordingly fixes the equivalent of silicium at 21·3.

In order, however, to prove the general validity of Kopp's observations, it was necessary to re-examine the boiling-points of corresponding chlorine and bromine compounds which exhibited discrepancies, and to extend the inquiry to as great a number of new compounds as possible.

Mr. Francis Baldwin Duppa has, at my suggestion, undertaken an investigation of this subject, and has already obtained some valuable results, which I beg to communicate to the Royal Society.

The bromine-compound of titanium was unknown. Mr. Duppa has produced this substance by passing a current of bromine over an intimate mixture of pure titanic acid and carbon. The reaction takes place at a bright red heat, and furnishes a brown liquid, which solidifies in the receiver to a crystalline mass. Distilled with an excess of mercury, which removes any free bromine that may be present, the bromide of titanium presents itself as an amber-yellow compound, exhibiting a magnificent crystalline structure; it attracts moisture with the greatest avidity, and is converted into titanic and hydrobromic acid. Bromide of titanium has a specific gravity of 2·6. The fusing-point was found, 39°. The boiling-point was examined by Mr. Duppa with a considerable quantity of substance, the purity of which had been ascertained by analysis. It was observed to be 230° C. The boiling-point of the chloride of titanium, as observed by Dumas, and confirmed by Mr. Duppa, is 135°. The difference, $230-135=95=3\times31\frac{1}{3}$, is exactly the same as that observed between the boiling-points of chloride and bromide of silicium.

This observation furnishes an additional support to the analogy of silicium and titanium, while it points unequivocally to the formulæ

$$TiCl_3 \text{ and } TiBr_3,$$

as representing the atomic constitution of these two compounds.

Titanic acid, hitherto universally represented as a binoxide TiO_2, would then assume the formula

$$TiO_3$$

in perfect analogy with that of silicic acid.

The equivalent of titanium would then be changed from 24·29, the number at present adopted, to 36·39. The protoxide of titanium would in this case become a sesquioxide, and the compound hitherto viewed as sesquioxide would have to be considered as an intermediate oxide—as a combination of the sesquioxide with the teroxide, in fact, as a bititanate of sesquioxide of titanium.

Formulæ of the Titanium Compounds.

Old Notation.		New Notation.
Ti=24·29		Ti=36·39.
TiO	First oxide	Ti_2O_3
Ti_2O_3	Second oxide	$Ti_4O_9=Ti_2O_3, 2TiO_3$
TiO_2	Acid	TiO_3
$TiCl_2$	Chloride	$TiCl_3$
$TiBr_2$	Bromide	$TiBr_3$.

It is scarcely necessary to observe, that an alteration of the equivalent of titanium on the ground of the difference of the two boiling-points, would be hazardous, if not supported by additional experimental evidence, and that further researches on the series of titanium are required in order to establish whether the proposed alteration actually affords a simpler expression for the combining relations of this remarkable element.

"On some new Colouring Matters." By Arthur H. Church and William H. Perkin.

Nascent hydrogen, acting upon an alcoholic solution of dinitrobenzole or of nitraniline, produces a crimson coloration, due to the formation of a new substance, to which we have given the name *nitrosophenyline.*

This new body presents some remarkable properties. It fuses below 100° C.; is uncrystallizable, and not volatile without decomposition; it dissolves in alcohol with an orange-red tint, and an alcoholic solution containing only ·2 per cent., although perfectly transparent to transmitted light, presents a flame-coloured luminous opacity in reflected light. Nitrosophenyline dissolves in hydrochloric acid, producing an intense crimson colour, which is changed to a yellowish-brown by alkalies and is restored by acids.

The analysis of nitrosophenyline has led us to the formula

$$C_{12}H_6N_2O_2,$$

which may be written thus:— $C_{12}\begin{matrix}H_6\\NO_2\end{matrix}N$, and so may be viewed as aniline, in which 1 equiv. of hydrogen is replaced by 1 equiv. of binoxide of nitrogen: the following equation sufficiently explains the formation of nitrosophenyline:—

$$C_{12}H_4 2NO_4+8H=C_{12}H_6N_2O_2+6HO.$$

We have produced from all the dinitro-compounds we have yet experimented upon, colouring matters similar to nitrosophenyline: the following is a list of such dinitro-compounds:—

1. Dinitrobenzole .... $C_{12}H_4 2NO_4$.
2. Dinitrotoluole...... $C_{14}H_6 2NO_4$.
3. Dinitroxylole ...... $C_{16}H_8 2NO_4$.
4. Dinitroxylole ...... $C_{18}H_{10} 2NO_4$.
5. Dinitrocymole...... $C_{20}H_{12} 2NO_4$.
6. Dinitronaphthaline.. $C_{20}H_6 2NO_4$.

We have examined minutely the colouring substance produced in the case of dinitronaphthaline. It proves to be perfectly analogous in composition with nitrosophenyline; in properties also it is similar; and from its alcoholic solution it may be obtained in crystals, having a lustre somewhat similar to that of murexide: its formula, as deduced from our analysis, is

$$C_{20}H_8N_2O_2,$$

which we may arrange thus:— $C_{20}\begin{matrix}H_8\\NO_2\end{matrix}N$, and so view it as naphthylamine in which 1 equiv. of hydrogen has been replaced by 1 equiv. of binoxide of nitrogen. This substance we term nitrosonaphthyline. It may likewise be obtained by the action of nitrous acid on naphthylamine, or of nitrite of potassium upon the hydrochlorate of naphthylamine: the following equations represent the three processes for its formation:—

1. $C_{20}H_6 2NO_4+8H=C_{20}H_8N_2O_2+6HO.$
2. $C_{20}H_9N+NO_3=C_{20}H_8N_2O_2+HO.$
3. $C_{20}H_{10}N, Cl+KNO_4=C_{20}H_8N_2O_2+2HO+KCl.$

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Conversion of the Acids of the Bile into the biliary Colouring Matter. By MM. FRERICHS *and* STÆDELER.

IT may be regarded as decided, that the urine of patients with jaundice contains no biliary acids, or mere traces of them, when abounding in pigment. In our former numerous experiments we were unable to detect biliary acids under these circumstances, and hence arrived at the same result as Griffith, Pickford, Gorup-Besanez, and Scherer.

Lehmann however observed that in well-marked jaundice, the biliary acids are often present in large quantity when the urine contains but little pigment. This observation, of the accuracy of which there can be no doubt, appeared to indicate an intimate relation between the acids and the colouring matters of the bile, and that when the excretion of the bile is impeded, the acids either pass into the urine in an undecomposed state, or are previously converted into colouring matter in the blood or some of the organs.

To determine this point, we first endeavoured to ascertain whether this conversion would take place out of the body, and were so successful that even our first experiments led to very interesting results.

Everyone who has studied the metamorphoses of the biliary acids knows how difficult it is to obtain the products of the action of mineral acids, especially dyslysine, in a colourless state, even when the material used is perfectly pure; we therefore first directed our attention to these coloured products, using sulphuric instead of muriatic acid for their production, as the amount obtained with the former is very small. We soon found however that the action of concentrated sulphuric acid upon the biliary acid is totally different from that of muriatic acid; chromogenic substances are produced, the reactions of which we shall now briefly describe, although we cannot at present lay down the composition of these products, nor the relation they bear to the biliary acids.

When strong sulphuric acid is added to pure glycocholate of soda, it coheres into a colourless resinous mass, which gradually dissolves in the cold to form a saffron-yellow mass, with heat becoming bright or brownish-red. Water precipitates colourless, greenish, or brownish flakes, according to the temperature at which the solution takes place. Neither the resinous mass formed at first, nor the flakes precipitable by water, consist of glycocholic or cholonic acid, as was once erroneously supposed; moderately dilute sulphuric acid appears however to decompose the glycocholic acid in the same manner as concentrated muriatic acid.

Glycocholic acid which has been altered by sulphuric acid, possesses the property of rapidly absorbing oxygen from the air, thereby passing into splendidly-coloured compounds. If the colourless amorphous mass produced by sulphuric acid, when freed as completely as possible from adherent acid, is placed upon a piece of filtering-paper, it deliquesces, and a ruby-red spot is produced, the edges of which soon become blue, and in a short time the whole is indigo-blue. In a few days this colour also disappears, and the spot becomes light brown. The paper appears to exert no influence upon this reaction, for the same change of colour is observed on the deliquescence of the amorphous mass upon glass or porcelain, except that it ensues somewhat less rapidly.

Solution of glycocholic acid in strong sulphuric acid contains the same chromogenic matter in solution, but the excess of acid impedes oxidation and the resulting coloration. If the solution be precipitated by water, and the flakes separated from the acid liquid be gently warmed in a water-bath, in a few seconds they become violet and blue. The change of colour is also very beautifully observed by moistening a piece of filtering-paper with water, then placing some of the acid liquid upon it, and drying it over a lamp. If the sulphuric acid acts for a longer time upon the biliary acid at the temperature of the water-bath, the spot upon the paper is green.

This reaction is often of use in detecting the biliary acid, as the smallest quantity of evaporated bile yields an intense reaction. With a view to the further examination of the blue product of decomposition of the glycocholic acid, we have made some other experiments upon decolorized ox-bile, from the alcoholic solution of which the greater part of the taurocholate of soda had been precipitated by æther.

The syrupy bile was mixed with 2 to 3 vols. of strong sulphuric acid, when it became warm and brownish-red. After having been heated for half an hour in a water-bath, the mass assumed a deeper reddish-brown colour, and by reflected light appeared bright grass-green. Water precipitated brown flakes, which when heated with access of air, became indigo-blue. The blue mass was insoluble in cold water, but at a boiling heat a brown solution was formed, from which on evaporation a product of decomposition separated, forming a dark brown membrane. The grass-green alcoholic solution of the brown colouring matter left on evaporation a greenish-blue residue, which became yellowish-brown when treated with potash, without dissolving in appreciable quantity. Acids, even dilute acetic acid, restored the original colour.

After heating the mixture of bile and sulphuric acid for six hours, essentially the same result was obtained. The blue mass in this case also became yellowish-brown with potash, was scarcely soluble in excess, and on the addition of acetic acid, again became greenish-blue. With hot acetic acid a bile-brown solution was formed, which on the addition of nitric acid immediately became bluish-green, then violet, and at last dirty yellow. Acetate of lead produced in the brown acetic solution a slightly coloured precipitate, which, when treated with nitric acid, also exhibited the change of colour. After the mixture of bile and sulphuric acid had been heated for eight days upon a moderately heated water-bath, a dark green mass, consisting of microscopic globules, had separated, which were insoluble in acid water, but soluble in pure water, with a deep green colour. In dilute potash it was perfectly soluble with a pure bile-brown colour, which, on the addition of nitric acid, first became green, then reddish, and finally yellow.

The above reaction of these products of decomposition with nitric acid resembles that of the natural colouring matter of the bile; the play of colours is however less lively, resembling that observed when icteric urine abounding in pigment is treated with nitric acid. We obtained, however, more favourable results on treating the amorphous precipitate thrown down from decolorized ox-bile by æther with sulphuric acid.

The dried gum-like mass was dissolved in a small quantity of water by heat, and sulphuric acid added in drops. A few drops only of the acid were sufficient to produce a splendid red colour, which by exposure to the air gradually passed into a blue. The solution of this colouring matter was not rendered turbid by water, and nitric acid produced the most beautiful play of colours, through violet, red, and pale brownish-yellow. When the biliary solution, coloured red by sulphuric acid, was mixed with more acid, the colour became brown. The precipitate now produced by water was not in dense flakes (as in the case of the glycocholic acid), but very delicate, and slowly subsided with a pale green colour.

When the acid liquid was poured off from it, and the residue gently heated, an intense green, blue, and violet colour was produced; the coloured products were perfectly soluble in potash with a brown colour, and the solution differed in no respect in its reaction with nitric acid from an alkaline solution of the colouring matter of the bile.

The red colour first produced by the action of sulphuric acid, and which gradually passes into blue, appears to indicate that the biliary mass precipitated by æther might be mixed with sugar, an acetate, or some substance yielding the reactions of Pettenkofer's bile-test. We were unable however to detect sugar in one experiment made on the small scale; although, if conversion of the biliary acids into colouring matter occurs in the organism*, as the facts mentioned above render probable, the sugar in the liver would probably be concerned in it. At present we confine ourselves to pointing out the resemblance between the natural colouring matter of the bile and the products of decomposition of the biliary acids which we have obtained. But we think it may be positively affirmed that the chromogenic substance, from which the blue colour is produced by oxidation, sometimes occurs in the liver, and apparently in the pancreas* also. We formerly enunciated the view, that this colouring matter might arise as an accessory product in the formation of glycocholic acid, tyrosine being resolved into glycocoll and saligenine in the liver, the glycocoll only being applied to the preparation of the bile; it is also possible that tyrosine, or more probably some isomeric compound, unites directly with a fatty acid to form glycocholic acid. The conjugate fatty acid would then be homologous with ricinic acid $= HO, C^{34} H^{31} O^{5}$. When copulated with the body isomeric with tyrosine, it would form glycocholic acid,—

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* More recent experiments have confirmed this view. About a drachm of pure colourless ox-bile, dissolved in distilled water, was injected into a dog. Six hours afterwards the animal passed about 3 oz. of dark brown urine, of spec. grav. 1·015, and with a slightly alkaline reaction. By repose it deposited a tolerably thick layer of green flakes, which appeared under the microscope as brownish-green granules. On the addition of nitric acid, the play of colours characteristic of the biliary pigment was beautifully displayed. Pettenkofer's test gave a negative result.

$$HO, C^{34} H^{31} O^{5} + C^{18} H^{11} NO^{6} = HO, C^{52} H^{42} NO^{11};$$

and when copulated with saligenine, cholic acid,—

$$HO, C^{34} H^{31} O^{5} + C^{14} H^{8} O^{4} = HO, C^{48} H^{39}, O^{9}.$$

The property of the last acid of losing water and passing into the resinous choloidic acid and dyslysine on boiling with acids, would be owing to the saligenine, which, as is well known, is also converted by the action of acids into the resinous saliretine with the loss of water. The share taken by the nitrogenous sulphuretted copula of the biliary acids in the formation of the colouring matters, cannot at present be laid down. It is certain however that our colouring matters, as well as those naturally found in the bile, contain nitrogen, but no sulphur. M. Cloetta of Zurich has recently made the interesting discovery, that Verdeil's pulmonic acid is nothing more than taurine; he obtained it in a perfectly pure state, and analysed it from the coagulated liquid of the lungs treated with acetate of lead. There can be no doubt that this taurine is connected with the taurocholic acid; but it would be hazardous to regard it as a product of decomposition of this acid, as it may equally be applied to its formation.—Müller's *Archiv* for January 1856.

On Tungsten and some of its Combinations. By A. Riche.

In the preparation of metallic tungsten the author had recourse to the reduction of tungstic acid by hydrogen, and the action of sodium on the chloride. A current of pure dry hydrogen is passed through a luted porcelain tube containing tungstic acid, which is kept at a red heat for two hours by means of coke broken into small pieces; the result is a mass which contains no oxygen. In operating at a lower temperature, there always remains a certain quantity of the lower oxides.

The tungsten thus produced is not fused, or even aggregated; it forms small crystalline grains, capable of acquiring a metallic lustre by friction; and of scratching glass with ease. When exposed to the heat of a furnace strong enough to soften the crucible, it remained solid, and it was only by means of a battery of 200 Bunsen's elements that the author succeeded in fusing it. In this case a considerable portion of the metal was oxidized, and burnt with a blue flame.

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* Archiv f. p. Anat. u. Phys., vii. 580.

Tungsten is not oxidized in the air, or even in dry oxygen, except at a very high temperature, and then the action is slow. It does not burn in dry chlorine, and its temperature must be brought to about 572° F. before the action commences. Nitric acid, kept at 158° or 176° for three or four days, converts it into tungstic acid. Nitro-muriatic acid acts a little more rapidly. Concentrated sulphuric and muriatic acids convert it into blue oxide, and at last this changes into tungstic acid.

Aërated, distilled, or common water appears to have no action upon tungsten, even by a contact of six weeks; this is also the case with alkaline water, whilst this same water containing a little sulphuric acid acquires a blue colour, but the action is very slow and weak. This metal does not act upon water at 212° F., but at a red heat the decomposition of water is effected with the greatest energy; the tungsten swells up, and is soon entirely converted into oxide.

When placed with iodide of æthyle in a sealed tube, and heated to about 464° F., the metal is scarcely altered by ten days of contact; nevertheless small nacreous needles are seen floating in the liquid; these are oxyiodide of tungsten. If iodide of methyle be substituted for that of æthyle, the action is more distinct; the liquid, when distilled, furnishes, besides unchanged iodide of methyle, a viscous liquid, which boils at a high temperature. When this is agitated with warm æther and alcohol, an oil separates, whilst the evaporation of the æther leaves a substance, which, when properly purified, crystallizes in large colourless laminæ, fusible at 230° F., and presenting the composition $3(C^2H^3)W, I$. This iodide, agitated with freshly precipitated oxide of silver, furnishes the oxide $3(C^2H^3)W, O$ in the form of a white powder.

This body combines with acids, forming uncrystallizable salts, which remain when concentrated in the form of a viscous liquid, from which alkalies precipitate the oxide. These salts are also produced by the action of acids upon the iodide.

To determine the equivalent of tungsten, the author employed the reduction of tungstic acid, WO^3, by hydrogen. The weight of water collected, and that of the residue of tungsten, led to the number 87, which is a little lower than that hitherto admitted; this is accounted for by a difference in the materials employed, that used in previous experiments having been prepared by means of carbonate of soda, and therefore not perfectly pure.

To obtain the so-called chloride of tungsten, the author directed a current of dry chlorine upon a mixture of 1 part of tungstic acid and 3 parts of powdered charcoal, placed in an earthenware bitubulated retort heated to dull redness. To obtain it in a state of purity, it is carefully distilled in a current of hydrogen, when, as it is more volatile than the other compounds produced, it readily separates from them.

This compound, heated with sodium in a tube filled with hydrogen, always furnished water and oxide of tungsten, from which the author was led to think that this supposed chloride contained oxygen; on analysis it gave numbers agreeing exactly with the formula WCl^2O. When treated with water, it is rapidly decomposed into tungstic and muriatic acids; if the experiment be made in a tube over mercury, it is found that no hydrogen is evolved. This reaction, which is inexplicable if we suppose the formula to be WCl^2, is easily understood if we adopt the formula given above. Thus—

$$WCl^2O+2HO=WO^3+2HCl.$$

The true chlorides of tungsten have not hitherto been recognized, because they are converted into the red oxychloride by the presence of the smallest quantities of water.

Terchloride of Tungsten.—This compound is obtained in abundance by passing a current of dry chlorine over pure tungsten placed in a heated porcelain tube, through which dry hydrogen is passed previously, to remove air and moisture. It crystallizes when sublimed in long steel-gray needles, which fuse at 424° F., furnishing a black liquid, which solidifies into a gray lump with the appearance and fracture of iodine. Water decomposes it immediately. Its analysis leads exactly to the formula WCl^3.

Bichloride of Tungsten.—It is prepared in very small quantities when the preceding chloride is placed in a glass tube and reduced by hydrogen. The operation is stopped when no more muriatic acid is evolved. There remains a small quantity of a blackish-brown product of the constitution WCl^2. It is rather difficult to keep within the limits of temperature required for this reaction. With too great a heat the terchloride is volatilized, and the product is contaminated with metallic tungsten, a portion of which is deposited on the walls of the tube in a beautiful specular ring.

Bisulphuret of Tungsten.—The sulphuret of tungsten corresponding with tungstic acid is easily obtained, but this is not the case with the bisulphuret. The author prepared it by heating equal weights of bitungstate of potash and sulphur in an earthenware crucible until the materials were in a state of quiet fusion. The residue is treated with water, which dissolves the tungstate of potash; the sulphuret is then washed upon a filter, and afterwards dried. It is a black substance, which crystallizes in small needles, and becomes oxidized at a red heat when in contact with air, or at 122° F. in presence of nitric acid. Its composition shows it to be bisulphuret of tungsten.—*Comptes Rendus*, Feb. 4, 1856, p. 203.

On some Cobalt Compounds. By P. SCHWARZENBERG.

Crystallized Protoperoxide of Cobalt.—When protoxalate of cobalt, obtained by the evaporation of its solution in ammonia containing muriate of ammonia, is calcined in an open platinum crucible, protochloride of cobalt is formed after the decomposition of the oxalic acid, with evolution of ammonia; and when the chlorine is expelled by long calcination in the air, the oxide of cobalt remaining only dissolves partially with evolution of chlorine in boiling concentrated muriatic acid, and there remains a grayish-black metallic residue, consisting of microscopic octohedra of protoperoxide of cobalt:—

	Calculated.		Found.
3 equivs. cobalt	88·5	73·44	73·86
4 equivs. oxygen........	32·0	26·56	26·37

These crystals are insoluble in boiling muriatic, nitric, and nitromuriatic acids; they are soluble completely, although with difficulty, in concentrated sulphuric acid, and dissolve readily, with a bluish colour, in fusing bisulphate of soda. They are not attracted by the magnet, are hard, brittle, and readily reduced to powder, and give a black streak.

When dry protochloride of cobalt is calcined in a current of oxygen gas or common air, the chlorine is driven off, and the cobalt and oxygen form a non-crystalline compound, which is soluble with evolution of chlorine in hot muriatic acid; this frequently contains intermixed microscopic crystals, which behave like those above described. By calcination with chlorate of potash or oxide of manganese, protochloride of cobalt also loses its chlorine and the cobalt is oxidized. When a dry mixture of protochloride of cobalt and muriate of ammonia is calcined in dry oxygen gas or atmospheric air, muriatic acid is driven off simultaneously with a cobalt compound, whilst another portion of the cobalt remains in combination with oxygen; this residue, besides the amorphous oxide, also contains crystals of the protoperoxide, which may be isolated by treatment with concentrated muriatic acid. The same final result is obtained by the calcination of a mixture of peroxide of cobalt and muriate of ammonia in oxygen gas, when chloride of cobalt is formed first of all, with simultaneous evolution of ammonia, at a moderate heat. The temperature has an essential influence upon the formation of the crystallized protoperoxide, as when too low a heat is employed all the cobalt forms an amorphous oxide, which is soluble with evolution of chlorine in hot concentrated muriatic acid. When protochloride of cobalt is calcined in aqueous vapour, muriatic acid escapes, and there remains only an amorphous protoxide, which is readily soluble in concentrated muriatic acid.

Cobaltate of Potash.—If the above-described protoperoxide, or protoxide, or protocarbonate of cobalt, &c., be put into fusing hydrate of potash, it dissolves with a beautiful blue colour as long as the potash still contains an excess of water; and when the cold mass is dissolved in water, an oxide of cobalt remains in brown flakes. If the fused mass be further heated in an open silver crucible, it becomes brown; and when it is kept for a short time at the temperature at which potash volatilizes, the dissolved cobalt compound is seen to crystallize from it on cooling. This remains, when the excess of potash is dissolved by means of water, in the form of thin six-sided prisms, and other, probably rhombic, forms. These crystals, which Becquerel took for protoxide of cobalt, are a compound of cobalt, oxygen, potash, and water.

If this compound, during its preparation, be heated long enough in the presence of the air, all the cobalt is found in the form of this compound, and the potash which has not entered into combination dissolves in water with evolution of oxygen, so that it is partially converted into peroxide. If, on the other hand, the calcination be not long enough continued, a portion of the cobalt separates in brown flakes on treatment with water, and the potash dissolves in that fluid without any evolution of oxygen. From this it appears that the formation of peroxide of potassium only commences when all the cobalt has taken up the quantity of oxygen necessary for the formation of the compound. The silver crucible in which the operation is carried on is only attacked when a portion of the potash has become converted into peroxide; and from this the fact is explained that in repeated preparations the crystals often contained silver, whilst in other cases they did not.

The largest and best developed crystals were obtained by the employment of 6 to 8 parts of hydrate of potash with 1 part of carbonate of cobalt, and when the fusing was not continued too long, so that in the subsequent treatment with water only a slight evolution of oxygen took place. When the fusion is continued longer with access of air, the crystals separate in the fused mass in proportion as the potash is converted into peroxide; so that it appears that hydrate of potash only, and not peroxide of potassium, is a solvent for this body.

The crystals are black, with a metallic lustre, very like micaceous iron ore; they are soft, give a black streak, are not attracted by the magnet, have no alkaline reaction, and are insoluble in water, but dissolve readily in concentrated acids,—in muriatic acid with a strong evolution of chlorine. Dilute muriatic acid does not act upon them in the cold, and does not extract the potash from them. At 248° to 266° F. the crystals lose about 18 per cent. of water; at 392° F. they still retain as much water as is required to form a hydrate with the potash which they contain. Even after this loss of water the compound has no alkaline reaction, but when more strongly heated they have a strong alkaline reaction, and the potash may then be extracted from them by means of water.

In the analysis of the compound, it was reduced by means of a dry mixture of carbonic oxide and carbonic acid, as in the reduction by hydrogen the amount of oxygen and water could not be separately determined; by this process all the water was driven off, and the potash was converted into carbonate of potash. The weight of expelled water was directly determined, the carbonate of potash was extracted by means of water from the weighed residue, and in the portion remaining undissolved the cobalt, a little carbon (taken up from the mixture of gases), and frequently a small amount of silver were found. The amount of oxygen could be calculated from the weight and composition of the residue remaining after the reduction, the loss of weight during this process, and the amount of water driven off.

The analyses (after deducting the small quantities of carbon and silver, as oxide of silver) led to the formula $KO, 3Co^3O^5 + 3HO$ for the compound when dried at 212° F., and $KO, 3Co^3O^5 + 2HO$ when dried at 266° F.:—

Dried at 212° F.	Found.			Calculated.
Cobalt	57·48	55·55	56·39	57·75
Oxygen	26·05	25·62	25·82	26·11
Potash	10·62	13·96	11·55	10·27
Water	5·80	4·34	6·11	5·87

Dried at 266° F.	Found.		Calculated.
Cobalt	57·23	58·11	58·91
Oxygen	26·42	26·33	26·62
Potash	12·71	10·74	10·47
Water	3·46	4·77	4·00

Schwarzenberg supposes that by longer fusion a portion of the potash (in consequence of the formation of peroxide) quits the combination, and is replaced by an equivalent quantity of water. He regards the formulæ above given as more probable than the supposition that cobaltic acid is CoO^2, according to which the compound dried at 212° F. must be regarded as—

$$\left.\begin{matrix}KO\\2HO\end{matrix}\right\} 3CoO^2 + 3(CoO, CoO^2) + HO,$$

and that dried at 266° F. as—

$$\left.\begin{matrix}KO\\2HO\end{matrix}\right\} 3CoO^2 + 3(CoO, CoO^2).$$

These formulæ correspond with the same per-centage amounts as those given above.—Liebig's *Annalen*, xcvii. p. 211.

On the Action of Phosphate of Soda on Fluor Spar at a Red Heat.

By H. Briegleb.

The author fused finely-powdered fluor spar with pyrophosphate of soda, which was obtained by the calcination of the ordinary phosphate of soda, $2NaO, HO, PO^5 + 24HO$, in several proportions with so much carbonate of soda that the phosphate of soda was present in the mass as $3NaO + PO^5$. His object was to try whether fluoride of sodium could be readily obtained in this manner, as it might be employed in the preparation of other fluorides with great advantage. The experiments were carried on in Liebig's laboratory at Munich.

Experiments were made,—1st, with a mixture of 2·5 parts of the salt $2NaO + PO^5$, 1 part $NaO\,CO^2$, and 2·25 parts of fluor spar;

2ndly, with a mixture in the proportions $CaO+2CaF+(2NaO+PO^5)$; 3rdly, with a mixture of $10CaF + 3(2NaO + PO^5) + 3(NaO, CO^2)$; 4thly, with a mixture of 4 parts of fluor spar, 5 parts of pyrophosphate of potash $(2KO+PO^5)$ and 2 parts of carbonate of potash. These mixtures were fused together in Hessian crucibles at a moderate red heat. The examination of the fused mass thus obtained showed that neither fluoride of sodium nor fluoride of potassium can be obtained in this way. In the first experiments with phosphate of soda, apatite was formed in crystals, and also some fluoride of sodium, although in very small quantity, so that this cannot be regarded as a method for the preparation of that body.

In testing the fused mass for fluoride of sodium, it was generally extracted by boiling water in a silver cup. In other cases, when the mass was extracted with warm water, and this solution was evaporated at a gentle heat, the author obtained the

New Double Salt, $(NaO)^3+PO^5+NaF+24HO$.—It crystallizes in octohedra belonging to the regular system, with subordinate occurrence of the surfaces of the cube and rhombododecahedron; they are hard, difficult of solution in water, and of a nauseous alkaline taste. They fuse in their water of crystallization; the residue decrepitates rather violently. Nitrate of silver gives a yellow precipitate in the solution of the salt, and the supernatant fluid is neutral. Sulphuric acid evolves much hydrofluoric acid from it. The salt has a specific gravity of 2·2165 at 77° F.; its saturated solution has a specific gravity of 1·0329 at the same temperature, and contains 1 part of the salt in 8·31 parts of water; its saturated solution at 158° F. has a specific gravity of 1·1091, and contains 1 part of the salt in 1·74 parts of water. Analysis gave:—

NaO	21·77	3	22·04
Na	5·38	1	5·45
F	3·50	1	4·50
PO^5	17·09	1	16·82
HO	52·25	24	51·19

The production of this salt explains why, in fusing fluor spar in the above proportions, only a part of it is decomposed and apatite is formed. It would seem therefore that a mixture of 1 part CaF to 2⅔ parts $NaO\,CO^2$ and 4 parts $2NaO, PO^5$ would be better adapted for the production of this double salt.

The author also obtained the same salt by mixing a solution of fluoride of sodium with one of ordinary phosphate of soda and caustic potash or soda, and also with a solution of phosphate of potash and caustic soda. In both the latter cases the double salt contained no potash. He also obtained it by digesting cryolite with a solution of phosphate of soda and caustic soda, and purifying the crystals by recrystallization from the alumina dissolved with them. —Liebig's *Annalen*, xcvii. p. 95.

On Furfurine. *By* L. Svanberg *and* C. E. Bergstrand.

The authors have investigated some salts of furfürine.

Bisulphate of Furfurine, $C^{30}H^{12}O^{6}N^{2}, HO, SO^{3}+HO, SO^{3}+7HO$, is a salt which effloresces at ordinary temperatures, and appears to be decomposed even at 176°–194° F. Its solution has an acid and bitter taste. The neutral salt was not obtained. When a tolerably concentrated solution of the acid salt, or its solution saturated with furfurine, is heated, a blackish-brown powder is deposited, and the solution contains a body which is not precipitated in a pulverulent form by ammonia, but separates in a tough mass, which, when kneaded together a little, acquires a stony hardness.

Phosphate of Furfurine, $(C^{30}H^{12}O^{6}N^{2}HO+2HO)+PO^{5}$, forms four-sided prisms, which undergo no loss of weight at 302° F., but fuse at 392°–419° F., forming a black glassy mass, which dissolves in hot alcohol, and then no longer gives the reaction of ordinary phosphoric acid.

Sesquiphosphate of Furfurine, $(2C^{30}H^{12}O^{6}H^{2}HO+HO)+PO^{5}$, was obtained by mixing a solution of 1 atom of the preceding salt with 1 atom of furfurine dissolved in alcohol, and heating and filtering the mixture. It formed oblique four-sided prisms, which when dry are stable in the air; it dissolves readily in boiling water and alcohol, but is nearly insoluble in æther. The crystals stand a heat of 338°–365° F. without decomposition, and behave like those of the preceding salt at a higher temperature. The solution of this salt is neutral.

Neutral Phosphate of Furfurine, $(C^{30}H^{12}O^{6}N^{2}HO)^{3}+PO^{5}$.—The solution of this salt has an alkaline reaction. Like the two preceding, it has a bitter taste.

Pyrophosphate of Furfurine, $(2C^{30}H^{12}O^{6}N^{2}, HO)PO^{5}+2HO$, is obtained by saturating pyrophosphoric acid with an alcoholic solution of furfurine. When dried in the exsiccator, it forms a crystalline glassy crust.

Metaphosphate of Furfurine.—The authors endeavoured to obtain this salt by treating freshly precipitated metaphosphate of baryta with a solution of neutral sulphate of furfurine. A gum-like mass was obtained from the fluid filtered from the sulphate of baryta.

Bitartrate of Furfurine crystallizes in oblique four-sided prisms from a moderately acid solution of furfurine in tartaric acid. When treated with potash, these crystals evolve ammonia, and no furfurine can be reproduced.

In connexion with these salts of furfurine, the authors refer to the peculiarities of the production and constitution of furfurine in comparison with other nitrogenous bodies. Furfurine and a small number of known compounds are formed of 3 atoms of an organic body and 2 atoms of ammonia, with the elimination of 6 atoms of water. These bodies are—

$3(C^{14}H^{6}O^{2})$, oil of bitter almonds
$+2NH^{3}-6HO=C^{42}H^{18}N^{2}$, hydrobenzamide.
$3(C^{14}H^{5}O^{2})\quad +2NH^{3}-6HO=C^{42}H^{15}N^{2}$, azobenzoyle.

$3(C^{10}H^{4}O^{4})$, furfurole
$+2NH^{3}-6HO=C^{30}H^{12}N^{2}O^{6}$, furfuramide.
$3(C^{16}H^{8}O^{4})$, hydruret of anisyle
$+2NH^{3}-6HO=C^{48}H^{24}N^{2}O^{6}$, anishydramide.
$3(C^{14}H^{6}O^{4})$, hydruret of salicyle
$+2NH^{3}-6HO=C^{42}H^{18}N^{2}O^{6}$, salicylimide.

To indicate the formation of these bodies, the authors propose to name these bodies *amlides* instead of *amides.—Oversigt af Kongl. Vetensk. Akad. Förhandl.*, 1854, p. 309.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Causes of the serious Loss of Silver which occasionally takes place during the Roasting of Silver Ores. By Prof. PLATTNER.

It has been long known from experience, that during the roasting of silver ores and furnace products in a finely divided state, in addition to the mechanical loss of silver through the formation of flue-dust, there also occurs a loss by direct volatilization, varying according to the properties of the ore from 1 to 10 per cent., and in argentiferous blende, exposed for a long time to a strong calcining heat, amounting to much more. These facts give rise to a question which may be divided into two parts, namely,—1st, How does it happen that in ores containing an equal per-centage of silver, but of different qualities and composition, the loss per cent. in silver differs when they are subjected to the process of roasting? and 2ndly, In what condition is the silver volatilized?

To solve the first part of this question, many experiments were made on the small scale by the author, in the following manner:—Various substances, for the most part quite free from silver, were reduced to a fine powder, and mixed with other substances rich in silver, and also in fine powder, in such proportion that the mixture should contain from 1 to 2 per cent. of silver; these were then exposed to the action of heat and atmospheric air in capsules of clay. For this purpose a muffle was used heated to dull redness, and with most of its openings closed so as to allow of a very moderate circulation of air within it. The heat was gradually raised until it reached the temperature at which sulphate of copper is slowly decomposed. The substances used to mix with those rich in silver were pyrites, blende, various anhydrous metallic sulphates and metallic oxides, and finely powdered quartz; those rich in silver were sulphuret of silver, light and dark Rothgiltigerz (pyrargyrite and proustite), metallic silver, sulphate, arseniate and antimoniate of silver, all in fine powder.

These substances were roasted from three-quarters of an hour to an hour and a half, and then assayed for silver in the usual way;

but in order to ascertain more accurately the amount of silver which should have been obtained from them, an equal amount of the unroasted ore was assayed with equal quantities of lead, so that the slight loss always occurring from the absorption of silver by the cupel ("Kapellenzug") would be the same in each case; the loss of silver during the roasting was then found by comparing the weight of the two buttons.

The results of these experiments showed—

1. That the loss of silver in question was occasioned chiefly by chemical causes.

2. That a volatilization of silver appeared to take place when the silver in the ore either passed from the state of sulphuret into that of metal, or when the oxide of silver in combination with sulphuric acid again suffered decomposition.

The loss appeared to be greatest in light, loosely aggregated substances whose particles had little cohesion and were not disposed to sinter together, as they were more readily penetrated and traversed by the atmospheric air.

3. That the loss of silver was greater when the roasting was protracted, if at the same time the temperature was increased.

4. That the loss was increased when magnetic oxide of iron or suboxide of copper exercised a reducing action on sulphate of silver.

5. That generally the loss of silver was greater when the silver existing as sulphate was exposed to a protracted roasting at a high temperature in company with free metallic oxides, than when it was present as arseniate or antimoniate of silver. The reason of this is, that the sulphate of silver is decomposed and reduced to metallic silver before either of the other salts, and more particularly before the arseniate, although their behaviour at a high temperature is not altogether the same, as the antimoniate of silver is very rapidly decomposed, the other two salts more slowly.

With regard to the second part of this question, In what condition is the silver volatilized? the following experiments on the small scale were instituted by the author:—

1. 3 grms. of silver, in a minute state of division, were carefully mixed in a glass mortar with an equal volume of finely powdered quartz, this mixture was introduced into a glass tube ½ an inch wide and about 20 inches long, of difficultly fusible glass. And after that part of the tube which contained the mixture had been enveloped with platinum foil in order to ensure a more uniform application of the heat, it was raised by means of a spirit-lamp to a moderate red heat (incipient *strong calcining* heat), while from a gasometer a current of dry hydrogen gas was passed slowly over it. Although this experiment was prolonged for upwards of an hour, not the slightest appearance of volatilization of the silver could be perceived. 2. An experiment conducted in the same manner with carbonic oxide, led to the same result. But 3. when a similar mixture was treated with oxygen gas, there quickly appeared in the neighbourhood of the mixture, towards the open end of the tube, a slight, dull, grayish-white coating, which

gradually increased, and extended about an inch along the tube; afterwards that portion of the coating nearest to the mixture was converted into a shining, annular, metallic crust. At the conclusion of the experiment, which like the former ones was carried on for an hour, a portion of the sublimate was removed, and on rubbing it in an agate mortar was found to be metallic silver, and this was confirmed by testing in the wet way. The part of the glass tube where the mixture had rested was found to be stained of a light to a dark yellow by oxide of silver, both above and below, and a little to the right and left of it. 4. A mixture of finely divided silver and ignited oxide of zinc, treated in the same manner with oxygen gas, gave in general the same results; the metallic coating, however, was not quite so striking; the tube also was found to be coloured yellow by oxide of silver where the mixture had rested.

From the results of the above experiments we may draw the conclusion, that that portion of the silver which, in addition to that carried off as flue-dust escapes during an oxidizing roasting, is removed, not in the metallic state, but at a certain temperature commencing at a low red heat, as oxide of silver, which afterwards, in its free state and at a low temperature, is again reduced to metallic silver; but as it then exists in such an extremely minute state of division, it becomes mixed with the gaseous products of the combustion of the fuel, and also the gases and vapours resulting from the oxidation of the ores, and is readily carried away with them into the atmosphere.—*Berg- und hüttenmann. Zeitung*, 1855, No. 35.

On a new Method of manufacturing Sugar from Beet-root, or other Saccahariferous Plants. By EMIL PFEIFFER.

The juice of the beet, obtained either by extraction or pressure in the usual way, is brought into the defecating pan and defecated with the necessary quantity of lime (0·3 to 0·4 per cent.), and then neutralized with superphosphate of lime. To 100 quarts of juice about 3 quarts of the acid phosphate of 4° B. are taken, or a proportionate quantity according to its degree of concentration, taking care however to leave the solution sufficiently alkaline to turn reddened litmus-paper distinctly blue. If, through error or want of caution, too much has been added, the evil may be remedied by the addition of milk of lime. According to the author, acid phosphate of lime has no decomposing action on solutions of sugar. The addition of the superphosphate causes a considerable precipitate, which is removed from the solution by the bag-filters. The solution is concentrated by evaporation to 18° B.; it then appears thick and clouded; this is increased by a further addition of superphosphate, taking care however to leave the solution slightly alkaline as before. The solution is again filtered, and then boiled best in a vacuum-pan. On crystallization, which is finished in ten hours, 50 to 60 per cent. of the amount of sugar is obtained as crystalline sugar for the first product.

The syrup which remains after the first product is diluted with water in the clarifying pan (or better with defecated juice) to 28° B., and mixed with a fresh quantity of milk of lime, about half the quantity used in the first defecation; and hereupon the liquid is heated, and treated with sufficient superphosphate to cause a considerable precipitate, which is separated by filtration as before. This precipitate contains a large quantity of colouring matter, and other substances such as alkalies, which are precipitated in the form of double salts. The syrup, thus clarified, is quite clear, but must still possess an alkaline reaction; it is now evaporated for the second crystallization, which is finished in forty-eight hours. The mass obtained contains 50 per cent. of sugar, polarizing 95 per cent. pure sugar.

The syrup remaining is again defecated with lime and superphosphate, whereby a precipitate of colouring matter and other foreign substances is produced. On filtration and evaporation, a third product is obtained. The syrup from this, on repetition of the process, furnishes a fourth and fifth product.

In like manner, viz. the alternate treatment with lime and superphosphate of lime, the author proceeds in the refining of sugar, and also in the treatment of the molasses and syrups produced by the methods in common use. The syrups from Indian sugar give by this process a considerable amount of sugar, which is not the case with the common methods, as they contain a large quantity of acetate of lime, which prevents the crystallization. This salt is decomposed by the superphosphate of lime*, and acetic acid is set free. An experiment, carried out on the large scale, at the sugar refinery of Carl Joest and Son of Cologne, on the syrup of colonial sugar, from which no more sugar could be extracted by crystallization, afforded, on treating it by the above method, 28 per cent. of crystalline sugar on the first operation, and would have yielded considerably more on further treatment.

The author has pursued this method for six weeks without trouble or difficulty in his manufactory at Ossendorf near Cologne, and found that beet has yielded in general within 1½ per cent. of the total amount indicated by polarization, which is to be sought for in the residue from the press and in the molasses.—*Kunst- und Gewerbebl. für Bayern.*, 1855, pp. 524–529.

[This process does not appear to me to differ from that recommended by Brande for neutralizing with phosphoric acid, made by digesting bone-ash with oil of vitriol and diluting with water. In point of fact, both use superphosphate of lime, and both direct that the solution of syrup should be left slightly alkaline. See "Otto's Landwirthschaftlichen Gewerbe," p. 666. The excess of lime used to be removed by sulphuric acid, but animal charcoal, which is found to decompose the saccharate of lime, is now universally employed for this purpose.—T. H. HENRY.]

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* How so if the solution be kept alkaline?

PROCEEDINGS OF SOCIETIES.

Royal Society.

Feb. 7, 1856. (Col. Sabine, R.A., V.P. and Treas., in the Chair.)

"Note on a new Class of Alcohols." By M. Aug. Cahours and A. W. Hofmann, Ph.D., F.R.S. &c.

On submitting to dry distillation glycerine, either alone or together with bisulphate of potassium or anhydrous phosphoric acid, M. Redtenbacher obtained a remarkable product, to which he gave the name of acroleine. Presenting all the characters of an aldehyde, and approximating more particularly to vinic aldehyde by the general aspect of its reactions, this substance changes under the influence of oxidizing bodies, especially of oxide of silver, an acid being formed, named by this philosopher acrylic acid, an acid which stands in the same relation to acroleine as acetic acid does to aldehyde.

The researches of MM. Will and Wertheim on the essential oils of mustard and of garlic, tended to indicate a relation between these substances on the one hand and acroleine and acrylic acid on the other, a result which was established by the more recent investigations of MM. Berthelot and De Luca. On studying the action of iodide of phosphorus on glycerine, these chemists obtained an iodine-compound named by them iodide of propylene, which is an analogue of the chloride and bromide of propylene, previously produced by MM. Cahours, Reynolds, and Hofmann, when submitting to the action of chlorine and bromine the gases which are formed when either amylic alcohol or valeric acid and its homologues are exposed to the influence of heat.

MM. Berthelot and De Luca have further shown that the result of the mutual decomposition of iodide of propylene and sulphocyanide of potassium is an oil identical with that obtained on distilling the seeds of black mustard with water in an alembic. By this remarkable experiment it is most clearly demonstrated that the volatile oil of mustard belongs to the propylene series, a relation which had been previously pointed out by Capt. Reynolds, but which he has omitted to establish by experiment. If, then, we admit the existence of a hydrocarbon, C_6H_5, analogous to ethyl, C_4H_5, we get

C_6H_5Cl	Chloride of propylene.	C_4H_5Cl	Chloride of ethyl.
C_6H_5Br	Bromide of propylene.	C_4H_5Br	Bromide of ethyl.
C_6H_5I	Iodide of propylene.	C_4H_5I	Iodide of ethyl.
C_6H_5S	Essential oil of garlic.	C_4H_5S	Sulphide of ethyl.
$C_6H_5C_2NS_2$	Essential oil of mustard.	$C_4H_5C_2NS_2$	Sulphocyanide of ethyl.
$C_6H_4O_2$	Acroleine	$C_4H_4O_2$	Aldehyde.
$C_6H_4O_4$	Acrylic acid.	$C_4H_4O_4$	Acetic acid.

All that now remained was to discover the keystone of this edifice, in other words, to establish the existence of an alcohol to which the preceding compounds might be referred, and by the aid of which a still more numerous series of ethers, both simple and compound, and analogous in every respect to the derivatives of ordinary alcohol, might be obtained. After many protracted and unsuccessful attempts, we have succeeded in producing the alcohol and ether of this series, for which we propose retaining the name of the acryl series.

In order to arrive at this result, we have submitted several silver-salts to the action of iodide of acryl. There are but few acids whose salts lend themselves conveniently to this reaction. Among the various salts which we have examined with this view, the oxalate of silver has furnished the most satisfactory results. This salt is most violently attacked by iodide of acryl; the reaction is complete after two or three hours' digestion. The *oxalate of acryl* formed in this process, when separated from the iodide of silver, washed with water, dried over chloride of calcium, and redistilled, presents itself as a colourless transparent liquid, heavier than water, possessing a peculiar aromatic odour. It boils at 207°, and by analysis has been proved to contain

$$C_8H_5O_4 = C_2(C_6H_5)O_4.$$

When treated with ammonia, oxalate of acryl furnishes oxamide and the alcohol, which was the object of our researches. This alcohol—*acrylic alcohol*—is a colourless transparent liquid of a peculiar, somewhat pungent odour, resembling that of mustard, and which in fact is more or less characteristic of nearly all the members of the acryl series.

The analysis of acrylic alcohol has led to the formula

$$C_6H_6O_2 = 4 \text{ vol. of vapour.}$$

This compound is isomeric with acetone and with propyl-aldehyde, from which substances, however, it differs essentially by the aggregate of its properties.

Acrylic alcohol burns with a much more luminous flame than ordinary alcohol. It mixes in all proportions with water. Treated with potassium, it disengages hydrogen and is converted into a transparent gelatinous mass, which is the *acryl-term corresponding to potassium-alcohol*.

This potassium compound is violently attacked by iodide of acryl; a precipitate of iodide of potassium is thrown down, and a liquid is formed lighter than water, and insoluble in this fluid. This new substance corresponds to ordinary ether; its formation is illustrated by the following equation:—

$$C_6(H_5K)O_2 + C_6H_5I = KI + C_{12}H_{10}O_2.$$

The same product is formed by the action of iodide of acryl upon oxide of silver or of mercury.

On treating the new potassium-alcohol with iodide of ethyl, or the ethyl-potassium-alcohol with iodide of acryl, an aromatic liquid is produced, which is obviously the *mixed ether of the ethyl and acryl series.*

If acrylic alcohol be distilled with chloride, bromide or iodide of phosphorus, the *chloride, bromide* and *iodide of the acryl series* are reproduced with the greatest facility.

Acrylic alcohol dissolves in concentrated sulphuric acid, without separation of carbon; the liquid, mixed with water and neutralized with carbonate of barium, furnishes a crystalline salt, which contains

$$C_6H_5BaS_2O_8 = BaSO_4, (C_6H_5)SO_4.$$

This is the *sulphovinate of the series.*

On treating the mixture of acrylic alcohol with concentrated sulphuric acid, a most violent reaction takes place; the alcohol is entirely carbonized with evolution of sulphurous acid.

Anhydrous phosphoric acid affects the alcohol with less energy. The mass darkens with evolution of a transparent colourless gas, burning with a luminous flame. The analysis of this gas remains to be made.

Acrylic alcohol is rapidly attacked by oxidizing agents. A mixture of sulphuric acid and bichromate of potassium acts with tremendous violence; the products of the reaction being acroleine and acrylic acid, or its products of decomposition. The same transformation is effected by spongy platinum.

When treated with potassa and bisulphide of carbon, the new alcohol solidifies at once into a mass of splendid yellow needles, which correspond to xanthate of potassium.

By the aid of the alcohol itself, its sulphovinic acid, or its iodide, all the terms of the acryl series may be produced with the greatest facility. We will specify the following compounds, the study of which we have more or less completed.

Acryl-oxamethane, or *oxamate of acryl,* is readily formed by adding alcoholic ammonia in small quantities to oxalate of acryl, until a permanent precipitate is produced. The filtered solution deposits on evaporation the oxamate in magnificent crystals.

Carbonate of acryl is an aromatic oily liquid, lighter than water. It is formed like the other carbonic ethers, by the action of sodium upon the oxalate. An alcoholic solution of this substance, when treated with baryta, furnished carbonate of barium and acrylic alcohol.

Benzoate of acryl is readily produced by the action of chloride of benzoyl upon acrylic alcohol. It is a liquid heavier than water, which boils at 220°, and possesses an aromatic odour, similar to that of benzoic ether. The analysis of this substance leads to the formula

$$C_{20}H_{10}O_4 = C_{14}[H_5(C_6H_5)]O_4.$$

The same body is easily produced by the mutual reaction of iodide of acryl and benzoate of silver.

Acetate of acryl, obtained by the action of iodide of acryl upon acetate of silver, is a liquid lighter than water, of an odour resembling that of common acetic ether. According to our analysis, it contains

$$C_{10}H_8O_4 = C_4H_3(C_6H_5)O_4.$$

Cyanate of silver is most violently attacked by iodide of acryl, even in the cold. The heat generated during this reaction is so powerful that the whole of the new product distils over. The substance thus obtained has an incredibly penetrating odour, and causes lacrymation in the highest degree. The analysis of this colourless transparent liquid, which boils at 82°, led to the formula

$$C_8H_5NO_2 = C_2(C_6H_5)NO_2.$$

This is the *cyanate of acryl.* Gently warmed with a solution of ammonia, this liquid readily dissolves, and the solution deposits upon evaporation magnificent crystals, which are nothing but acrylic urea

$$C_8H_8N_2O_2 = C_2H_3(C_6H_5)N_2O_2$$

corresponding to thiosinnamine, the long-known sulphur-urea term of this series,

$$C_8H_8N_2S_2 = C_2(H_3, C_6H_5)N_2S_2.$$

Aniline produces with cyanate of acryl an analogous substance, which crystallizes remarkably well.

When treated with water, cyanate of acryl is gradually converted into a solid crystalline substance. The compound obtained in this manner has the composition and all the properties of *sinapoline* or *diacrylic urea*. Its formula is

$$C_{14}H_{12}N_2O_2 = C_2[H_2(C_6H_5)_2]N_2O_2,$$

and its formation is illustrated by the following equation:—

$$2\underbrace{C_8H_5NO_2}_{\text{Cyanate of acryl.}} + 2HO = \underbrace{C_{14}H_{12}N_2O_2}_{\text{Sinapoline.}} + 2CO_2.$$

Cyanate of acryl is decomposed by a concentrated solution of potassa; a solid substance is rapidly formed, which floats upon the surface of the solution, and which is nothing but the same sinapoline, whilst a strongly alkaline liquid passes into the receiver, which is a mixture of several bases, in which we have traced already

(1) Methylamine.
(2) Propylamine.
(3) Acrylamine.

The latter substance boils between 180° and 190°. All our attempts to produce a well-crystallized platinum-salt of this base have hitherto failed.

The experiments detailed in the preceding sketch incontestably demonstrate the existence of a new series of alcohols, the third term of which is acrylic alcohol.

Like ordinary alcohol, this new alcohol furnishes a series of derivatives, which may be formulated in a similar manner.

The following tables exhibit the terms of the acryl series hitherto prepared in juxtaposition with the corresponding members of the ethyl series:—

Acryl Terms.		Ethyl Terms.
$C_6H_6O_2$	Alcohol	$C_4H_6O_2$
C_6H_5O or $C_{12}H_{10}O_2$	Ether	C_4H_5O or $C_8H_{10}O$
C_6H_5Cl	Chloride	C_4H_5Cl
C_6H_5Br	Bromide	C_4H_5Br
C_6H_5I	Iodide	C_4H_5I
C_6H_5S or $C_{12}H_{10}S_2$	Sulphide	C_4H_5S or $C_8H_{10}S_2$
$C_2(K, C_6H_5)S_4O_2$	Xanthate of potassium	$C_2(K, C_4H_5)S_4O_2$
$C_2(C_6H_5)NS_2$	Sulphocyanide	$C_2(C_4H_5)NS_2$
$C_2(C_6H_5)NO_2$	Oxycyanide or cyanate	$C_2(C_4H_5)NO_2$
$C_2(H_3C_6H_5)N_2S_2$	Sulphuretted acryl-urea—Thiosinnamine	?
$C_2(H_3, C_6H_5)N_2O_2$	Acryl-urea, Ethyl-urea	$C_2(H_3, C_4H_5)N_2O$
$C_2[H_2(C_6H_5)_2]N_2O_2$	Diacryl-urea, Diethyl-sinapoline-urea......	$C_2[H_2(C_6H_5)_2]N_2O_2$

Acryl Terms.		Ethyl Terms.
$C_2(C_6H_5)O_4$ or $C_4(C_6H_5)_2O_8$	Oxalate	$C_2(C_4H_5)O_4$ or $C_4(C_4H_5)_2O_8$
$C_4H_2(C_6H_5)O_4$	Oxamate............	$C_4(H_2, C_4H_5)O_6$
$C(C_6H_5)O_3$ or $C_2(C_6H_5)_2O_6$	Carbonate	$C(C_4H_5)O_3$ or $C_2(C_4H_5)_2O_6$
$C_4H_3(C_6H_5)O_4$	Acetate	$C_4(H_3, C_4H_5)O_4$
$C_{14}H_5(C_6H_5)O_4$	Benzoate	$C_{14}H_5(C_4H_5)O_4$
$C_6H_5SO_4HSO_4$	Sulphovinic acid ..	$C_4H_5SO_4HSO_4$
$(C_6H_5)H_2N$	Acrylamine, Ethylamine	$(C_4H_5)H_2N$
$C_6H_4O_2$	Aldehyde. Acrylic, Ethylic, Acroleine	$C_4H_4O_2$
$C_6H_4O_4$	Acid. Acrylic; acetic	$C_4H_4O_4$
C_6H_6	Hydrocarbon. Propylene ?, Acetene	C_4H_6

Acrylic alcohol, the history of which we have endeavoured to sketch in the preceding pages, and in the study of which we are now engaged, is the third term of a series of alcohols, which is parallel to the ordinary alcohols of the formula

$$C_{n2}H_{n2+2}O,$$

and the prototype of which is ethylic alcohol. The acid corresponding to this alcohol is acrylic acid, as has been stated. Chemists are already acquainted with several homologues of acrylic acid, which stand to the series of fatty acids in the same relation which exists between our new alcohol and common alcohol. Cyanide of acryl, which is readily procured by the action of iodide of acryl upon cyanide of silver, but which as yet we have not been able to obtain in a state of perfect purity, when submitted to the action of potassa, will obviously furnish an acid, homologous to acrylic acid equally as cyanide of propyl is transformed into butylic acid.

We terminate this note with a synoptical table of the two homologous groups.

Group of Alcohols.				Group of Acids.			
$C_2H_2O_2$		$C_2H_4O_2$	Methylic	C_2O_4	(Carbonic ?)	$C_2H_2O_4$	Formic
$C_4H_4O_2$		$C_4H_6O_2$	Ethylic	$C_4H_2O_4$		$C_4H_4O_4$	Acetic
$C_6H_6O_2$	Acrylic	$C_6H_8O_2$	Propylic	$C_6H_4O_4$	Acrylic	$C_6H_6O_4$	Propionic
$C_8H_8O_2$		$C_8H_{10}O_2$	Butylic	$C_8H_6O_4$		$C_8H_8O_4$	Butylic
$C_{10}H_{10}O_2$		$C_{10}H_{12}O_2$	Amylic	$C_{10}H_8O_4$	Angelic	$C_{10}H_{10}O_4$	Valeric
$C_{12}H_{12}O_2$		$C_{12}H_{14}O_2$	Caproic	$C_{12}H_{10}O_4$		$C_{12}H_{12}O_4$	Caproic
$C_{14}H_{14}O_2$		$C_{14}H_{16}O_2$		$C_{14}H_{12}O_4$		$C_{14}H_{14}O_4$	Œnanthylic
$C_{16}H_{16}O_2$		$C_{16}H_{18}O_2$	Caprylic	$C_{16}H_{14}O_4$		$C_{16}H_{16}O_4$	Caprylic
—		—		—		—	
—		—		—		—	
$C_{36}H_{36}O_2$		$C_{36}H_{38}O_2$		$C_{36}H_{34}O_4$	Oleic	$C_{36}H_{36}O_4$	Stearic

This table exhibits a considerable number of gaps, which the progress of science will not be long in filling up. Even now we have established by experiment that bromide of amylene suffers many changes, which are perfectly analogous to those which we have witnessed in the acryl series, and even the derivatives of olefiant gas appear to exhibit in many respects an analogous deportment.

THE CHEMICAL GAZETTE.

No. CCCXXV.—May 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Behaviour of some Acids in the Animal Organism.

By C. BERTAGNINI.

THE conversion of benzoic acid into hippuric acid, which takes place when the former is introduced into the animal organism, and the analogous conversion of nitrobenzoic acid into nitrohippuric acid, induced Bertagnini to ascertain how far some other organic acids are altered when taken internally.

Crystallized *camphoric acid* could be taken in doses of 0·5 grm. without the least injury; 12 grms. were taken in the course of two days. The urine passed during this period was strongly acid, and contained unaltered camphoric acid. After it had been evaporated to one-third of its original volume and mixed with muriatic acid, it became turbid, and a small quantity of a crystallized substance separated; a further portion of this was dissolved by æther when this was shaken with the urine, and separated in brown crystals when the æther was evaporated. By treating these with milk of lime, decomposing the soluble salt produced with muriatic acid, and recrystallizing the separated substance from water, several grammes of a perfectly white non-nitrogenous acid were obtained; it possessed all the properties, and also the composition of camphoric acid:—

	Found.	Calculated ($C^{20}H^{16}O^{8}$).
Carbon	60·01	60·00
Hydrogen	7·93	8·00

Anhydrous Camphoric Acid, obtained by the distillation of camphoric acid and recrystallization of the product from alcohol, could be taken in doses of several grammes without any injurious action. The urine passed during its administration had a strong acid reaction, and furnished ordinary camphoric acid by the treatment above detailed. Anhydrous camphoric acid consequently undergoes no change in passing through the organism, except that it takes up two equivs. of water.

Salicylic Acid was taken in hourly doses of 25 centigrms., continued for two days, during which period about 6 grms. of the acid were taken. On the first day no ill symptoms appeared, but on the second there was continual singing in the ears and a sensation of stupefaction. The same symptoms occurred in a second experiment;

in which salicylic acid was given in similar doses, and in the whole to the amount of 7·5 grms. Only an hour after taking the first dose, the urine acquired a violet colour on the addition of salts of iron; this property increased during the course of the experiment, and was perceptible, although but slightly, two days after its completion. The urine was acid, as is usually the case. It was evaporated to a small volume; the fluid was separated from the salts, strongly acidified with muriatic acid, and repeatedly agitated with æther; the ætherial solution, when evaporated, left a strongly acid watery fluid, and this, on further concentration, furnished crystals, which were purified by pressing, recrystallization from boiling water, and treatment with animal charcoal. The crystalline substance thus obtained however proved to be a mixture of fine needles, with thick and shining acicular crystals, the latter of which were volatilized by heat, whilst the former were decomposed at a high temperature, leaving a carbonaceous residue. The two portions could be completely separated by heating them to 284° to 302° F. in a current of air, when the volatilizable portion proved to be salicylic acid. The non-volatile substance was obtained in pure crystals from its solution in boiling water, to which a little animal charcoal was added. It contained nitrogen, and its composition was $C^{18}H^9NO^8$. Analysis:—

	Found.		Calculated.
Carbon	55·59	55·75	55·38
Hydrogen	4·77	4·86	4·61
Nitrogen	7·44	..	7·17
Oxygen	32·20	..	32·84

This composition agrees with the supposition that salicylic acid, like benzoic and nitrobenzoic acids, enters into a conjugate compound with glycocoll in the organism; thus—

$$\underset{\text{Salicylic acid.}}{C^{14}H^6O^6} + \underset{\text{Glycocoll.}}{C^4H^5NO^4} - 2HO = \underset{\text{New acid.}}{C^{18}H^9NO^8}.$$

The decompositions of the new acid also agree with this view. If it be boiled only for a few minutes with fuming muriatic acid, it crystallizes without alteration on the cooling of the fluid. But when boiled for several hours with muriatic acid, it is decomposed, and salicyclic acid may then be extracted by æther from the fluid after this has been neutralized by fragments of carbonate of lime; in this decomposition glycocoll is also set free.

The new acid, for which Bertagnini proposes the name of *salicyluric acid*, in allusion to the similarity of its constitution with that of hippuric acid, crystallizes from its hot aqueous solution in thin shining needles, concentrically grouped. It has a bitter taste, and a strong acid reaction. It dissolves abundantly in boiling, but sparingly in cold water; it is readily soluble in alcohol, and moderately so in æther. Its solution possesses the property of colouring persalts of iron violet in a high degree; the colour disappears on the addition of concentrated acids. It fuses at about 320° F. without loss of weight, and solidifies on cooling into an indistinctly crystalline mass. At about 338° F. it begins to acquire a brown colour, and to become decomposed, with volatilization of salicylic acid; with a stronger heat the mass swells up, evolves ammonia, and leaves a coal, which may be burnt without residue.

Salicyluric acid appears to resist the action of alkalies in a higher degree than that of acids. By boiling it for hours with an excess of baryta-water, only an inconsiderable evolution of ammonia is produced, and the acid remains essentially unaltered. When the aqueous solution of the acid is boiled with peroxide of lead, the latter is decolorized and the acid decomposed; on the cooling of the fluid, small shining needles separate.

Salicyluric acid readily forms well-crystallizable salts. With the aid of heat it decomposes the carbonates of lime and baryta with effervescence; its compounds with these bases crystallize from the filtrate. The baryta-salt forms thick, hard, transparent prisms, and is difficult of solution in cold water; the crystals lose water when heated, and then fuse, becoming decomposed at the same time, with carbonization and evolution of ammonia, together with an oily fluid, which smells like phenole. The lime-salt forms needles, is but slightly soluble in cold water, and insoluble in alcohol. There is another lime-salt, insoluble in water, which was obtained by the careful addition of small quantities of milk of lime to a hot solution of salicyluric acid; at a certain point the fluid sets into a mass consisting of shining laminæ, which do not dissolve in boiling water. Bertagnini supposes that salicyluric acid is a bibasic acid.

Anisic Acid, of which about 6 grms. were administered in two days, without any consequence except a feeling of weight in the stomach, passed off in the urine without alteration. The urine had an acid reaction, and when evaporated and mixed with muriatic acid, furnished anisic acid to æther with which it was agitated; this, when purified by recrystallization from water and treatment with animal charcoal, had the composition,—

	Found.	Calculated ($C^{10}H^8O^6$).
Carbon	63·16	63·15
Hydrogen	5·42	5·26

Liebig's *Annalen*, xcvii. p. 248, extracted from *Il Nuovo Cimento*, i. 363.

On the Equivalent of Antimony. By R. SCHNEIDER.

The equivalent of antimony has hitherto been assumed, according to the determination of Berzelius, at 1613 (or 129 for H=1). By a series of careful experiments, with which I am still occupied, I have convinced myself that this number has been taken far too high, and must be reduced by at least 100.

For reasons which I shall hereafter detail, I have made use of a natural compound of antimony in these experiments, namely, a sulphuret of antimony of unusual purity. It contained no foreign matters except a little quartz, which indeed could not be completely got rid of by mechanical means, but the quantity of which could be accurately determined in each experiment.

The reduction of this native sulphuret of antimony in a current of pure hydrogen gas was employed as the basis for the determination of its equivalent. This reduction can be carried out with certainty, and almost completely, at a temperature at which scarcely a perceptible trace of sulphuret of antimony is volatilized, always supposing that the current of hydrogen is not too rapid. In my previous experiments on the reduction, about an hour has been bestowed upon each gramme of sulphuret of antimony. Taking into account an extremely small quantity of sulphuret of antimony (in different experiments 0·0005 to 0·00125 grm.) which had escaped with the sulphuretted hydrogen gas into the receivers attached, and an inconsiderable quantity of sulphur (0·001 to 0·007 grm.), which was obstinately retained by the reduced antimony, the loss of weight observed in the reduction gave the composition of the sulphuret of antimony. In six experiments, in which the sulphuret of antimony was employed in quantities of from 3 to 10 grms., the amounts obtained were,—

71·427 to 71·519 per cent. of antimony, and
28·573 to 28·481 per cent. of sulphur,

or on the average 71·469 per cent. of antimony and 28·531 per cent. of sulphur. From this the equivalent of antimony may be calculated as very nearly 1503 (or 120·25 for H=1).—Poggendorff's *Annalen*, xcvii. p. 485.

On the Preparation of the Chlorides and Bromides of the Organic Radicals by the Action of Protochloride and Protobromide of Phosphorus upon the corresponding Monohydrated Acids. By A. Béchamp.

Two processes have been employed in the preparation of the chlorides corresponding with the anhydrous monobasic acids.

1. M. Cahours* made use of the reaction of perchloride of phosphorus upon the monohydrated acids, a process which is only applicable to the preparation of chlorides the boiling-point of which is superior to that of oxychloride of phosphorus.

2. M. Gerhardt† employed the reaction of protochloride of phosphorus upon the potash-salts of the monobasic acids.

The author has studied the action of protochloride of phosphorus upon the monohydrated monobasic acids and their æthers. From his experiments it appears that protochloride of phosphorus acts upon the monohydrated acids as it would do upon a mixture of anhydrous acid and water, and upon the æthers of these acids, as though these compounds actually contained in their molecule both the groups of the acid and æther, the chloride corresponding with water or with the acid and that corresponding with æther are obtained. Upon this he has founded a method of preparation for these chlorides, which appears to be of general application, convenient, and cheap.

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* Chem. Gaz., vol. vi. p. 417. † Ann. de Chim., xxxvii. p. 294.

If R be the oxygenated radical of an anhydrous monobasic acid, and RO the general formula of the corresponding anhydrous organic acid, the quantity of elements to be employed will be given by the following equation:—

$$2RO\,HO+PCl^3=ClH+PO^3\,HO+2RCl.$$

This is the result of the two following equations:—

$$6RO,HO+PCl^3=PO^3\,3HO+3ClH+6RO;$$
$$6RO+2PCl^3=2PO^3+6RCl.$$

The proof of these is to be found in the facts, that when these quantities are employed the organic chloride is very readily obtained quite free from protochloride of phosphorus, and in quantity nearly equal to that indicated by theory, whilst the residue is entirely composed of solid phosphorous acid. Anhydrous acetic acid itself gives a double decomposition with protochloride of phosphorus, furnishing chloride of acetyle; and it is remarkable that this decomposition takes place with more ease and rapidity than with the monohydrated acid, so that in a mixture of anhydrous and monohydrated acids the former is the first decomposed. The author adduces this in support of the view that the decomposition of the monohydrated acid takes place in two steps, and supposes that the same thing may occur with the other acids, which however he has not yet tried.

Protobromide of phosphorus behaves exactly like the protochloride; it sets free hydrobromic acid, and produces the corresponding bromide.

Oxychloride of phosphorus also reacts upon the monohydrated acids, but with less energy than the perchloride, and perhaps less than the protochloride. The residue is not trihydrated phosphoric acid, but a mixture of trihydrated acid precipitable in the form of ammonio-phosphate of magnesia, and of metaphosphoric acid, which directly precipitates chloride of barium, coagulates albumen, and gives a white precipitate with nitrate of silver, so that, as with the protochloride of phosphorus, by combining the two phases in one equation, we get—

$$6RO,HO+3PCl^3O^2=PO^5\,3HO+2PO^5+3ClH+6ROCl.$$

By means of the protochloride and protobromide of phosphorus the author has obtained with great ease the chlorides of cinnamyle, benzoyle, valeryle, butyryle, propionyle, and acetyle, and the bromides of valeryle, butyryle, and acetyle; or those of such compounds whose boiling-point is very high, but low when distilling the monohydrated acids with the chloride or bromide of phosphorus. The protochloride of phosphorus, boiling at 174° F., should possess a boiling-point sufficiently high or low to be decidedly different from that of the organic chloride, of which the boiling-point is superior or inferior to its own. The most disadvantageous case is when the organic chloride has a boiling-point very near that of the protochloride of phosphorus, as is the case with chloride of propionyle, which boils at about 176° F.; but this difficulty may be got over by employing a slight excess of propionic acid, so as to make sure of decomposing the whole of the protochloride of phosphorus, as it appears that the organic chlorides with a low boiling-point may be safely distilled in presence of the corresponding monohydrated acids.

The organic chlorides, from chloride of acetyle to that of valeryle inclusive, may be easily prepared by putting into a retort furnished with a receiver the proportions of monohydrated acid and protochloride of phosphorus indicated in the first equation. There is rarely any evolution of heat on mixing the substances, and the disengagement of muriatic acid soon commences, even in the cold with acetic acid. Heat is then applied with the water-bath, 104° F. for acetic acid, 176° F. at first and afterwards 212° F. for valerianic acid, and intermediate temperatures for the others. The temperature is maintained as long as there is any evolution of muriatic acid; the water-bath is then removed, and the volatile product of the reaction is distilled by the open fire. If the boiling-point of the chloride be near 212° F., the residue consists of very white phosphorous acid; if it be higher, the phosphorous acid is altered and red phosphorus separates. A single rectification will give a pure product. The boiling-point of chloride of valeryle is between 239° and 248° F. at a pressure of $0{\cdot}75^{m}$; its density at $42^{\circ}{\cdot}8$ F. is 1·005, so that it does not sink to the bottom of water like the chlorides which precede it in the series. In preparing the chlorides of cinnamyle, benzoyle, &c., the dry acid must be put into a mattrass furnished with a pointed tube; the proportionate quantity of protochloride of phosphorus is then added, and the whole is heated gradually from 140° F. to 248° F. as long as any muriatic acid is evolved. As soon as heat is applied the mixture liquefies; at the close it forms two strata—the lower one is phosphorous acid contaminated with red phosphorus, the upper one is the organic chloride; the latter is decanted and rectified. It is not advisable to distil the chlorides with a high boiling-point in presence of the phosphorous acid, for at the close the mass swells up greatly, and there is a sudden evolution of phosphuretted hydrogen, arising from the decomposition of the hydrated portion of the phosphorous acid.

The author has prepared the bromides of acetyle, butyryle, and valeryle, by distilling protobromide of phosphorus with the corresponding monohydrated acids in the proportions indicated by the equation—

$$2RO\,HO + PBr^3 = PO^3\,HO + BrH + 2RBr.$$

The organic bromides are obtained almost in the quantity indicated by theory. The protobromide does not dissolve in acetic acid, but does so in the others. The reaction takes place with the same facility as with the protochloride, but at a rather higher temperature; it commences at 194° and terminates at 212° F. for bromide of butyryle, and commences at 212° and only terminates at 248° F. for bromide of valeryle. When the evolution of hydrobromic acid ceases, the distillation is effected in presence of the phosphorous acid produced. This remains perfectly white in the preparation of the first two bromides, but becomes partially decomposed and yellow in that of bromide of valeryle, which boils at about 257° F.—*Comptes Rendus*, Feb. 4, 1856, p. 224.

On Anisoic Acid. *By* H. LIMPRICHT.

It is generally supposed that by the action of nitric acid upon oil of anise, anisaldehyde or anisylous acid and oxalic acid are first formed, and the following formula has been proposed to represent the decomposition—

$$\underset{\text{Anisoïne.}}{C^{20}H^{12}O^{2}} + 12O = \underset{\text{Anisaldehyde.}}{C^{16}H^{8}O^{4}} + \underset{\text{Oxalic acid.}}{C^{4}H^{2}O^{8}} + 2HO.$$

From the following experiments it appears probable that another product is first formed, which still contains 20 equivs. of carbon, and this only furnishes anisaldehyde and oxalic acid by the continued action of the nitric acid. Several years ago I repeatedly observed the production of a peculiar compound, when oil of star-anise was heated with nitric acid of spec. grav. 1·2 only until it sank to the bottom of the acid; if it were then agitated with a hot solution of bisulphite of soda, the aqueous solution on cooling did not deposit sulphite of anisaldehyde-sodium, but a soda-salt of the composition $C^{20}H^{17}NaO^{12}$. I have only just been able to complete the investigation of this compound in concert with M. Ritter.

For the acid, the soda-salt of which is obtained in the manner above described, I propose the name of *anisoïc acid*; its constitution, as deduced from the analyses of its salts, is $C^{20}H^{18}O^{12}$, and its production from anisoïne is according to the following equation—

$$\underset{\text{Anisoïne.}}{C^{20}H^{12}O^{2}}+6HO+4O=\underset{\text{Anisoïc acid.}}{C^{20}H^{18}O^{12}}$$

Although this acid has only been prepared from the oil of star-anise, there can be no doubt that the other oils containing anisoïne (such as the oils of anise, fennel, &c.) will furnish it when similarly treated.

Anisoïc acid, separated from the salt of silver or baryta by means of muriatic or sulphuric acid, crystallizes in small laminæ when the aqueous solution is evaporated; if a concentrated solution be allowed to stand long in the air, small but tolerably thick prisms are deposited. It is very soluble in water, alcohol, and æther, and it is therefore difficult to obtain it in good crystals; it has a strongly acid reaction, and its melting-point is about 248° F. When heated upon platinum-foil, it becomes brown, evolves fumes with an empyreumatic and anisaldehyde-like odour, and burns at last with a pale luminous flame; even when carefully heated, it cannot be sublimed without decomposition.

On one occasion, when a solution of the silver-salt mixed with muriatic acid had been accidentally evaporated to dryness in contact with the chloride of silver, a sublimate consisting of white needles had been deposited upon the latter; from its appearance it consisted of anisic acid, and this supposition was confirmed by the analysis of a small portion of the silver-salt.

0·0698 grm. of the silver-salt furnished 0·0295 grm. of silver.

	Calculated.	Found.
Anisate of silver contains	41·7 per cent. of silver.	42·2

An attempt to obtain anisic acid by heating free anisoic acid, moistened with a little muriatic or sulphuric acid, miscarried; only the products of decomposition, which are furnished by anisoic acid when heated alone, made their appearance. As we only possessed a few grammes of material, we could not obtain the acid sufficiently pure for analysis.

Anisoate of Soda, $C^{20}H^{17}NaO^{12}$ (dried at 212° F.).—The mode of preparation has been already described. The salt was obtained perfectly white by repeated recrystallization from a small quantity of hot water; it forms indistinct crystals, united into verrucose masses. It is readily soluble in water. 0·0589 grm., dried at 212° F., furnished 0·0163 grm. of sulphate of soda.

	Calculated.	Found.
Anisoate of soda contains	8·9 per cent. of sodium.	8·9 per cent.

Anisoate of Baryta, $C^{20}H^{17}BaO^{12}$ (dried at 212° F.).—The solution of the soda-salt was mixed with a sufficient quantity of sulphuric acid for its decomposition, and evaporated to dryness on the water-bath; the residue was extracted with absolute alcohol, and this solution, after being mixed with water, was digested with carbonate of baryta until it was neutralized. The filtered solution furnished on evaporation readily soluble warty masses, similar to those of the soda-salt.

Of the salt dried at 212° F.—

I. 0·4945 grm. furnished 0·187 grm. of sulphate of baryta.
II. 0·4525 ... 0·172 ... ...
III. 0·1156 ... 0·0449 ... ...
IV. 0·2015 grm., burnt with chromate of lead, gave 0·293 grm. of carbonic acid, and 0·0968 grm. of water.
V. 0·155 grm., burnt with chromate of lead, gave 0·223 grm. of carbonic acid, and 0·0773 grm. of water.

	Calculated.		I.	II.	III.	IV.	V.
C^{20}	120	39·8	..	..	..	39·65	39·23
H^{17}	17	5·6	..	..	..	5·33	5·54
Ba	68	22·5	22·16	22·27	22·75		
O^{12}	96	32·1					

Anisoate of Silver, $C^{20}H^{17}AgO^{12}$.—This was prepared both by the decomposition of the baryta-salt with sulphate of silver and by digesting the acid with carbonate of silver. It is readily soluble in water, forms warty crystals, and easily acquires a blackish colour when it is moist. This ready decomposability is the cause of a rather considerable difference between the numbers obtained by calculation and by the analysis of the salt dried over sulphuric acid:—

	Calculated.		Found.
C^{20}	120	35·2	34·1
H^{17}	17	4·9	4·0
Ag	108	31·6	32·2
O^{12}	96	28·4	

Liebig's *Annalen*, xcvii. p. 364.

On Anilotic Acid. *By* R. Piria.

With regard to the action of nitric acid upon salicine, Piria* had stated that when weak acid (from 15° to 20° B.) is employed, helicine or helicoïdine is produced; by the employment of a stronger acid (24° B.), the result is a nitrogenous acid, very similar to nitrosalicylic acid, characterized as anilotic acid; and by varying the concentration of the acid and the temperature, also nitrosalicylic and picric acids; and lastly, with concentrated nitric acid, picric and oxalic acids are produced. H. Major†, by shaking 1 part of salicine with 10 parts of nitric acid of 20° B. in a closed flask at 50° to 59° F., prepared a solution from which he obtained crystals which separated but slowly, and for the most part dissolved in æther, leaving only a little helicine; the ætherial solution furnished yellowish crystals of an acid, the properties of which agree with those given for anilotic acid, especially in its striking a blood-red colour with the persalts of iron. From the composition of the silver-salt $=AgO, C^{14}H^{4}(NO^{4})O^{5}$, Major declared anilotic acid to be identical with nitrosalicylic acid. Upon this Piria himself took occasion to republish ‡ his complete investigation of anilotic acid, which, although given to the world in 1846, in the 'Annali delle Università Toscane,' vol. i. p. 134, does not appear to have become known out of Italy.

According to this, the formation of anilotic acid depends less upon the concentration of the nitric acid employed than upon the presence of hyponitrous acid, which is produced by the first action of the acid upon the salicine. For the preparation of anilotic acid, a weak acid, saturated with nitrous oxide and therefore rich in hyponitrous acid, is to be preferred; when concentrated acid is employed, the anilotic acid is obtained contaminated with some nitrosalicylic acid, from which it is difficult to free it entirely. Into a stoppered bottle, 1 part of powdered salicine and from 6 to 8 parts of nitric acid of 20° B. are put, and the bottle is closed so as to prevent admission of air, and placed in a cool place; the nitrous oxide produced by the first action being unable to escape, causes the formation of hyponitrous acid, which gives a green colour to the fluid, and after some time crystals of anilotic acid separate. If, on the other hand, the action be allowed to take place in an open vessel, under similar circumstances in other respects, the fluid only acquires a yellow colour, and helicine is formed.

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* Liebig's Annalen, lvi. p. 65.

† Das Laboratorium der Universität Christiania (1854), p. 84; Liebig and Kopp's Jahresber., 1854, p. 628.

‡ Il Nuovo Cimento, ii. 299.

Anilotic acid crystallizes in long, thin, pointed prisms; it has an astringent and very bitter taste, but is inodorous. It dissolves but sparingly in cold water, but rather more freely in warm water, separating from this solution in crystals. In boiling water it dissolves partially, but the portion remaining undissolved loses its water of crystallization, and becomes converted into a heavy crystalline powder. It dissolves readily in alcohol and æther.

The aqueous solution of anilotic acid is colourless, reddens litmus strongly, and acquires a yellow colour on the addition of alkalies. It does not precipitate the salts of copper, silver, mercury, baryta, lime, zinc, manganese, or magnesia, or the neutral lead-salts, but gives a yellow precipitate with basic acetate of lead. With salts of peroxide of iron it gives an intense red colour, without forming a precipitate.

Concentrated sulphuric acid does not act upon anilotic acid in the cold; but when heated, dissolves it without decomposition, and deposits it on cooling in small crystals containing no water of crystallization.

The crystallized acid contains 12·8 per cent. of water of crystallization, which is volatilized in the air at 212° F., and *in vacuo* at ordinary temperatures. The acid, freed from water of crystallization, fuses, when heated, into a clear fluid, which solidifies in a crystalline form on cooling. When distilled, a portion of it is volatilized and a part decomposed, leaving a carbonaceous residue, which burns at last with a slight explosion.

Anilotic acid forms salts which are for the most part soluble and crystallizable. The neutral salts are white, those with an excess of base yellowish. On the addition of an acid to the yellowish solutions the colour disappears, and the anilotic acid separates in white voluminous flakes.

Analyses showed the composition of the dried acid to be $HO, C^{14}H^{4}NO^{9}$, and that of the crystallized acid $HO, C^{14}H^{4}NO^{9}+3HO$.

	Dried acid.			Crystallized acid.		
	Found.		Calculated.	Found.		Calculated.
C	45·75	45·63	45·95	40·00	40·00	40·00
H	3·00	2·93	2·73	4·21	3·93	3·86
N	7·69	7·69	7·65	..	..	6·67
O	43·56	43·75	43·67	..	..	49·47

Anilotic acid has consequently the same composition as nitrosalicylic acid. Nevertheless Piria regards them as distinct, and founds his opinion upon the following differences. Nitrosalicylic acid, prepared from indigo, is readily soluble in boiling water, and separates from this solution on cooling in crystals free from water of crystallization; it forms crystallizable yellow salts with potash and ammonia, and a soluble salt with oxide of silver. Anilotic acid dissolves but sparingly in boiling water, and when in contact with this is for the most part converted into a crystalline powder, free of water of crystallization; in its crystallized state it contains 3 equivs. of water of crystallization, and it forms white salts with potash and ammonia, and an insoluble salt with oxide of silver.—Liebig's *Annalen*, xcvii. p. 253.

Researches on Iodized Propylene, Allyle, and Allylic Compounds.
By MM. BERTHELOT *and* DE LUCA.

In a former memoir*, the authors showed that glycerine, treated with iodide of phosphorus, gave rise to iodized propylene, $C^6 H^5 I$, a substance remarkable for its chemical activity. It readily yields its iodine to the various agents with which it may come in contact, and thus produces a great variety of new compounds, sometimes by substitution and sometimes by simple or double decomposition. In this respect it is allied to the hydriodic æthers of the ordinary alcohols, and assists in general in the same reactions.

The authors have already shown† that hydrogen might be substituted for the iodine of iodized propylene to form propylene, and that by treating it with sulphocyanide of potassium, it was converted into iodide of potassium and oil of mustard. The results of their further investigations are as follows:—

1. By double decomposition with the salts of silver, iodized propylene forms iodide of silver and conjugate compounds analogous to the æthers. M. Zinin has lately obtained compounds of the same kind.

2. Iodized propylene, decomposed by oxide of mercury, produces an oxygenated compound analogous to æther. When decomposed by potash, dissolved in alcohol, amyle or glycerine, it forms mixed æthers analogous to those of Mr. Williamson.

3. Iodized propylene, decomposed by sodium, loses its iodine, and forms a carburet of hydrogen analogous to æthyle. To this carburet the authors give the name of *allyle*, applied long since by MM. Wertheim and Will to the natural oils of garlic and mustard.

I. *Action of the Salts of Silver.*—By the reaction of 1 equiv. of iodized propylene and 1 equiv. of dry butyrate of silver, a liquid is obtained, which is volatile about 293° F., and analogous in odour and in all its characters with ordinary butyric æther. It is *allylobutyric æther.*

With benzoate of silver, iodized propylene forms iodide of silver and a neutral compound of greater density than water, which is soluble in æther, volatile at 446° F., and exactly similar to ordinary benzoic æther. It is *allylobenzoic æther*, already described by M. Zinin. At 212° F. potash slowly decomposes this æther, reproducing benzoic acid and a volatile liquid, which is inflammable and miscible with water. With tartrate of silver, iodized propylene forms iodide of silver, and a compound soluble in æther, *allylotartaric æther.* When decomposed by sulphocyanide of potassium or silver, it gives *allylosulphohydrocyanic æther*, which is identical with oil of mustard.

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* Chem. Gaz., vol. xii. p. 448 (1854).

† See Chem. Gaz., *l. c.*, and vol. xiii. p. 288.

II. *Action of Oxide of Mercury and of the Alkalies.*—Iodized propylene, treated at 212° F. with dry oxide of mercury, gives rise to a peculiar fluid, volatile at 185° to 190° F., endowed with an ætherial and penetrating odour, which is to a certain extent analogous to that of radish. This liquid appears to be *allylic æther*.

At 212° F. alcoholic solution of potash decomposes iodized propylene, and gives origin to a compound, which is volatile at 144°·5 F., and appears to be *allylæthylic æther*. With potash and amylic alcohol it forms in the same way *allylamylic æther*, which is volatile at about 248° F.

A mixture of potash, glycerine, and iodized propylene gives rise to a liquid of a most disagreeable odour, which is soluble in æther, and volatile at 269°·6 F. The analysis of this body led distinctly to the formula—

$$C^{24}H^{20}O^{6}=C^{6}H^{8}O^{6}+3C^{6}H^{5}I-3HI,$$ *triallyline.*

The preceding facts show that iodized propylene presents the same general reactions as the hydriodic æthers, and that it forms, by double decomposition, conjugated bodies analogous to the æthers. The formula of the bodies thus produced is determined, almost with certainty, by the very conditions of their formation; but the numerous analyses made by the authors do not agree exactly with the probable formulæ of the substances obtained, the purification of which is extremely difficult. The obstacles are due to the constant simultaneous formation of accessory products, both fixed and volatile, and usually of gaseous propylene in considerable amount. It is to be observed also that the allylic compounds are not produced by the simple action of two direct affinities, but by a roundabout way, by inducing the formation of a very stable body (iodide of silver), and, as it were, forcing the other elements to remain in combination.

The following experiment proves this instability of the allylic compounds, even under those influences in the midst of which they were formed. If we attempt to produce these bodies by the reaction of butyric, benzoic, or stearic acid upon allylic æther, between 392° and 482° F., in sealed tubes, a process by which the æthers of various alcohols may be prepared, a large quantity of inflammable gases is developed, with production of a black ulmic substance and of a neutral butyric æther.

III. *Action of Sodium.*—The action of sodium upon iodized propylene produces iodide of sodium, and a perfectly definite hydrocarbon, *allyle*, $C^{6}H^{5}$:—

$$C^{6}H^{5}I+Na=C^{6}H^{5}+NaI.$$

Allyle is a very volatile liquid, endowed with a peculiar ætherial and penetrating odour, analogous to that of radish. It burns with a very luminous flame, and boils at 138°·2 F. Its density is =0·684 at 57°·2 F. The density of its vapour, determined at 212° F., was found =2·92; so that the formula $C^{6}H^{5}$ represents 2 vols. of vapour (density calculated, 2·89), the same as that of æthyle, methyle, &c.

Allyle mixes with sulphuric acid with evolution of heat; if all increase of temperature be avoided, the mass scarcely acquires any colour, but at the close of a few hours a great part of the modified hydrocarbon always separates, and floats on the surface. Hydrochloric gas is not sensibly absorbed by allyle. Fuming nitric acid changes it into a neutral liquid compound, which is soluble in æther.

The action of the halogenous bodies is especially remarkable. Allyle combines with chlorine, forming a liquid compound of greater density than water, with evolution of muriatic acid. It combines instantaneously with bromine, with evolution of heat. If the action be arrested at the moment when the liquid begins to acquire colour under the influence of an excess of bromine, and to evolve a little hydrobromic acid, and the mixture be then treated with potash, *bromide of allyle*, $C^6 H^5 Br^2$, is obtained; this is a crystalline compound, which is very soluble in æther. It is volatilizable without decomposition. It fuses at 98°·6 F., and sometimes remains liquid at ordinary temperatures.

Iodide of Allyle, $C^6 H^5 I^2$, is prepared by dissolving 6 or 7 parts of iodine in 1 part of allyle gently heated; the mixture liquefies at first, but in two or three minutes again becomes solid. The mass is triturated with an aqueous solution of potash, and the iodide of allyle is crystallized from boiling æther. This body is decomposed when boiled with potash in solution in alcohol; it furnishes a product the odour of which is analogous to that of allyle. When boiled with potash in water, it only undergoes an insensible decomposition, and evolves traces of inflammable gas. When heated with a mixture of fuming muriatic acid and mercury, it is slightly attacked, and does not evolve gases in appreciable quantities.

The formula of iodide of allyle, $C^6 H^5 I^2$, only differs by 1 equiv. of iodine from that of iodized propylene, $C^6 H^5 I$; and the authors have therefore tried to transform one of these bodies into the other, or to prepare iodized propylene by means of allyle. But none of their experiments succeeded.

1. By the action of 3 parts (1 equiv.) of iodine upon 1 part (1 equiv.) of allyle, the crystallized iodide, $C^6 H^5 I^2$, is formed, and the mixture retains the odour of allyle; when heated with mercury and fuming muriatic acid, no gas is evolved, but only the excess of liquid allyle.

2. Iodized propylene dissolves a large quantity of iodine with the assistance of heat; but treatment with an aqueous solution of potash removes this iodine, and reproduces the iodized propylene with all its characters. Moreover, in the conditions under which it is formed, iodized propylene is in the presence of an equivalent of free iodine, with which it does not combine.

3. Fuming muriatic acid and mercury transform iodized propylene into propylene, whilst they have no action upon iodide of allyle. The latter, when distilled, furnishes iodine and a neutral liquid, which is not converted into propylene by mercury and fuming muriatic acid.

These different facts prove that iodized propylene, $C^6 H^5 I$, and iodide of allyle, $C^6 H^5 I^2$, have not the same mutual relations as, for example, the two iodides of mercury; they correspond with two distinct molecular states.

Thus the carburet liberated by the action of sodium upon iodized propylene does not present the same relations to the latter that are presented by a true radical towards its iodide; for in the former case the results of analysis are not confirmed by synthesis.

On the other hand, allyle presents these relations towards bromide of allyle; for bromide of allyle, treated with sodium, reproduces allyle with all its properties, as odour, boiling-point, power of forming a crystallized compound with iodine, &c.—*Comptes Rendus*, Feb. 4, 1856, p. 233.

ANALYTICAL CHEMISTRY.

New Volumetric Determination of Chlorine in its Combinations.

By Dr. Mohr.

Levol has described a means of determining chlorine by a solution of silver, in which he renders the completion of the precipitation perceptible by an addition of phosphate of soda, the presence of an excess of silver being indicated by the yellow tint of the precipitate. The author has found that by this means the results are always too high, in consequence of the very slight colour of the phosphate of silver, which requires to be present in considerable quantity to become visible in the precipitate of chloride of silver.

The author accordingly tried arseniate of soda, and obtained much better results, from the brownish-red colour of the arseniate of silver, but soon passed from this to chromate of potash, which afforded results beyond his expectations.

When phosphate, arseniate, carbonate, or chromate of silver is mixed with solution of chloride of sodium, there is an instantaneous formation of chloride of silver and of another soluble salt. At the same time the colour of the insoluble silver-salt disappears; and the higher this is coloured the smaller is the quantity of it that may be recognized, and the more perceptible is the transition to the colourless or light yellow condition. But if a drop of silver solution be present above the quantity of the metallic chloride, the blood-red colour of chromate of silver makes its appearance distinctly. If 0·2 cub. centim. too much of the silver solution be added, the mixture is more than distinctly red. If chromate of potash were colourless, the phænomenon would be still more striking. But even in this case the formation of chromate of silver is perceived with a single drop of normal silver solution. The solution must not be acid, as then chromate of silver is not formed, or only in very small quantities, and besides bichromate of potash has a rather red colour. A slight excess of pure carbonate of potash, on the contrary, is not injurious, because then only the pale yellow colour of chromate of potash can be exhibited. Much carbonate of silver is disadvantageous, as carbonate of silver has no striking colour, although it is decomposed by metallic chlorides.

Two burettes filled with normal solutions are placed close together; an undetermined quantity of fluid is allowed to run from the burette with chloride of sodium, and the red colour is then produced by the addition of silver solution. The two burettes are then read off. A few cubic centimetres of a solution of neutral chromate of potash were added. The following numbers were obtained:—

Solution of chloride of sodium.	Solution of silver.
4·2 cub. centims.	4·3 cub. centims.
6·7 ...	6·8 ...
11·0 ...	11·1 ...
12·0 ...	12·1 ...
17·65 ...	17·75 ...
18·2 ...	18·3 ...
25·85 ...	25·95 ...
26·0 ...	26·1 ...

Thus in every case an additional $\frac{1}{10}$ cub. centim. of silver solution was employed, and this was exactly the quantity above that necessary for precipitation, but required to indicate its completion. When solution of chloride of sodium is dropped in until the disappearance of the reddish colour, both burettes stand exactly even.

The author then employed this method with weighed portions of metallic chlorides, and obtained the following numbers:—

0·2 grm. of chemically pure and perfectly dry chloride of sodium =34·4 cub. centims. of silver solution; on the other hand, 0·1 cub. centim. of chloride of sodium=34·3 cub. centims. of silver solution =0·20051 grm. of chloride of sodium.

0·2 grm. chloride of potassium=1. 26·8 cub. centims. silver solution.
2. 26·8 ... ...
=0·19985 grm. of chloride of potassium.

0·2 grm. of chloride of ammonium=1. 37·35 c. c. silver solution.
2. 37·25 ... ...
This gives,—1. 0·19967 grm. chloride of ammonium.
2. 0·199138 ... ...

These experiments prove that alkaline chlorides may be determined with great accuracy by this method. The author has also employed it with urine, well-water, mineral waters, saltpetre, potashes, soda, and chlorate of potash, and always obtained concordant results. The amount of chlorine in a mineral spring may be determined at the well itself.

The chlorides of barium, calcium, mercury, &c., are precipitated with carbonate of soda; and if the precipitate be colourless, immediately tested with the silver solution, without filtration.—Liebig's *Annalen*, xcvii. p. 335.

On the Employment of Hyposulphite of Soda in Analytical Chemistry. By Dr. W. Vohl.

The author recommends, with Himly, the more frequent employment of hyposulphite of soda in analysis, instead of sulphuretted hydrogen. According to him it can also be used to evolve sulphu-

-retted hydrogen; if a piece of zinc is placed in dilute hydrochloric acid, and a few drops of a solution of hyposulphite of soda added, sulphuretted hydrogen is evolved. If now to this mixture a solution of a salt of lead, bismuth, cadmium, &c. is added, the sulphurets of the corresponding metals are precipitated.—*Ann. der Chem. und Pharm.*, vol. xcvi. pp. 237 to 243.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On some Constituents of Madder, and of the Products obtained from it, especially on the Pectine Bodies contained in it. By Paul Schützenberger.

The author has instituted various experiments with madder, with the view of coming to some conclusion as to the pectine bodies contained in it. Madder from Avignon was extracted with four times its weight of water by maceration for ten minutes at 59° F. The extract furnished a moderate flocculent precipitate with alcohol, and on standing deposited a gelatinous mass, although in no great abundance; this had taken up the colouring matter. The precipitate produced by alcohol is, according to the author, pectate of potash, and the extract of madder contains no pectine. Under the name of "pectic acid" the author includes pectosic acid, pectic acid, and parapectic acid (which however is soluble in water); and under the name of "pectine," the pectine, parapectine, and metapectine of Fremy, as he leaves it undecided which of these particular matters is present in each case. This appears from the fact that the extract gives a flocculent precipitate with muriatic acid, and the fluid filtered from this is no longer precipitated by alcohol. The gelatinous mass formed when the extract is left to stand is pectic acid, the separation of which is probably induced by another organic acid which is formed in the extract. Alsatian madder, treated in the same way, gave the same results, but it contained much more pectic acid than the Avignon madder.

When madder is boiled for a few minutes with water containing muriatic acid, the extract mixed with alcohol, the precipitate thus produced dissolved in hot water, and this process repeated until the separation of the colouring matter, a colourless gelatinous body is obtained, which behaves like pectine. As however no pectine was found in the madder itself, the author concludes that the latter contains pectose, and that pectine is formed from this body by the action of the muriatic acid. Pectose was thus found in Alsatian and Avignon madder, and in madder flowers, but not in garancine. The author has determined the amount of pectose in the madder from the weight of the pectine, dried at 212° F., obtained by boiling madder for five minutes with water containing muriatic acid (50 cub. centims. muriatic acid to 1 litre of water), which he supposes to have the same composition as pectose; in this way he has found in Avignon madder 2·3, in Alsatian madder 2·13, and in madder flowers

1 to 1·05 per cent. of pectose. The smaller quantity of pectose in the madder flowers is accounted for by the fact that in their preparation a portion of the pectose is converted into pectine by the action of the acidulated water, and is removed in this form by washing.

The author also tried whether the madder contained any pectic acid besides the small quantity which is present in combination with potash. For this purpose he treated the madder extracted by acidulated water with solution of soda of 5°. The alkaline extract gave an abundant, flocculent, gelatinous precipitate with muriatic acid; this took up all the colouring matter. When the muriatic acid was allowed to mix very slowly with the fluid by pouring it carefully upon the bottom of the vessel, the whole fluid set into a gelatinous mass, in consequence of the gradual separation of the pectic acid; this is just like the jelly formed in the water in which certain samples of madder have been macerated. The pectic acid precipitated by muriatic acid was freed from the colouring matter by extraction with wood-spirit; but it was then coloured brownish by a humus-like body. To get rid of this, the pectic acid was dissolved in weak ammonia at a gentle heat, the solution was filtered, and the pectic acid then thrown down again by muriatic acid, when it was tolerably pure. Madder, therefore, as well as madder flowers, contains, besides pectose, pectic acid, which is contained in it in small proportion as pectosic acid.

If powdered madder be treated with solution of soda of 5° at 194° F., and washed until the water runs away colourless and no longer contains pectic acid, the residue is still of a strong violet-red colour. If this residue be treated with water containing muriatic acid, assisted by heat, and then again with solution of soda, the latter again extracts a large quantity of colouring matter and pectic acid, by which means the residue is entirely freed from colouring matter, and acquires the appearance of sawdust. This result is explained by the author as owing to the presence of a certain quantity of pectate of lime in the madder. This, and not, as has been supposed, the woody fibre, retains a portion of the colouring matter, so that it is not extracted by alkali; and it is not until the pectate of lime is decomposed by muriatic acid, that the colouring matter can be completely extracted with the pectic acid.

The author endeavoured to determine the amount of pectic acid in madder. For this purpose the madder was treated first with solution of soda, then with water containing muriatic acid, and afterwards again with solution of soda. The pectic acid was precipitated from the two alkaline extracts by muriatic acid, purified by the above-described treatment with wood-spirit and ammonia, and then dried at 212° F. Avignon madder, dried at 212°, treated in this manner, furnished, on the average of six very concordant experiments, 9·5 per cent. of pectic acid. If we deduct from this the 2·3 per cent. of pectose found in this description of madder, which is also converted into pectic acid by this process, it appears that Avignon madder contains 7·2 per cent. of pectic acid, of which, according to the author, about 2 per cent. are combined with lime. In the same way the author found that after the deduction of the pectose, Alsatian madder contained 6·4 per cent. of pectic acid, of which about 1 per cent. is combined with lime. In madder flowers he found on the average 10·5 per cent. of pectic acid. The amount of this acid combined with potash in the madder, which is the cause of the aqueous extract of madder becoming slimy or gelatinous by standing, is not more than 0·2 per cent. according to the author.

After the discovery of these large quantities of pectine bodies in madder, which have hitherto been regarded more or less as woody fibre, the author proceeded to determine the amount of the latter substance in madder. With this view he dried and weighed the residue of the treatment with solution of soda and muriatic acid just described, and deducted from the weight thus obtained, the amount of ashes left on the combustion of the residue; the remainder was considered to be pure woody fibre. In this way he found that Avignon madder, dried at 212° F., contained 19 to 19·5 per cent. of woody fibre, whereas, according to previous analyses, in which it is probable pectose and pectic acid were taken for woody fibre, the amount of this body was supposed to be 33 to 35 per cent. Alsatian madder contained 23, and madder flowers 30 per cent. of woody fibre.

In garancine, dried at 212° F., subjected to the same treatment, the author found 16·5 per cent. of pectic acid (for the most part free, but partly combined with lime) and 48 per cent. of woody fibre, which was less changed than is generally supposed. If we suppose that madder furnishes 40 per cent. of its weight of garancine, and that it contains 20 per cent. of woody fibre, the amount of the latter contained in the garancine should be 50 per cent. The number 48 obtained consequently indicates that the woody fibre undergoes no considerable loss of weight in the preparation of garancine. A similar calculation, supposing the garancine to be prepared from Avignon madder, which appears to be the case, shows that it should contain 18 per cent. of pectic acid, if no portion of this be destroyed in the preparation of garancine. The product occurring in commerce under the name of *alizarine* also contains pectic acid partly free and partly combined with lime, but its amount does not exceed 5 per cent. The woody fibre obtained from this was black, and had undergone a far greater change than that of garancine.

When 10 grms. of Avignon madder were boiled with water, 18 cub. centims. of carbonic acid were expelled; and by subsequently heating it with diluted muriatic acid, 66 cub. centims. were driven off. According to the author, this carbonic acid is combined with lime in the madder; and he supposes that the carbonic acid expelled by boiling with water is contained in it in the form of bicarbonate. The 66 cub. centims. of carbonic acid represent 0·27 grm., or 2·7 per cent. of the weight of madder, of carbonate of lime. In the ashes of the same madder the author found 5·7 per cent. of carbonate of lime, from which it is to be supposed that a quantity of lime corresponding with 3 per cent. of carbonate is combined with organic acids, and especially with pectic acid. The whole of the lime in garancine and madder-lake, and nearly the whole in commercial alizarine, which is found in their ashes, is also combined with organic acids. It is remarkable that both garancine and madder-lake, although prepared by the treatment of madder with concentrated sulphuric acid, still contain pectic acid and pectate of lime.

According to the author, the woody fibre and free pectic acid cannot hold back the colouring matter of the madder. Pectate of lime however appears to do this energetically. If pectate of lime be artificially produced by double decomposition, by means of an alkaline solution containing colouring matter, the latter passes into the gelatinous precipitate, and cannot be extracted therefrom either by alkali or wood-spirit. The solubility of the colouring matter of madder in cold water, according to the author, is to be ascribed to the presence of pectate of potash. According to the author, madder also contains the nitrogenous ferment to which Fremy has given the name of *pectose*, both in the soluble and in the insoluble state; in the latter however in the largest amount. The analyses of ashes given by the author are as follows. All the substances were dried at 212° F.:—

10 grms. of Avignon madder gave 1·363 grm. of ashes, of which
  0·300 grm. was soluble in water, consisting of chloride of potassium and a very little carbonate of potash, and
  1·063 grm. insoluble in water, in which were found
    0·29 grm. silica,
    0·572 grm. carbonate of lime,
    0·193 grm. phosphate of lime (precipitated by ammonia from the solution in muriatic acid).
10 grms. of madder flowers gave 1·263 grm. of ashes, of which
  0·077 grm. was soluble in water. This portion consisted of
    0·068 grm. sulphate of lime, and
    0·009 grm. chloride of potassium;
  1·185 grm. insoluble in water, containing
    0·328 grm. silica,
    0·624 grm. carbonate of lime,
    0·170 grm. phosphate of lime.
10 grms. of garancine gave 1·775 grm. of ashes, of which
  0·106 grm. was soluble, and consisted of CaO, SO^3, and
  1·669 grm. insoluble, containing
    1·02 grm. silica,
    0·448 grm. carbonate of lime, and
    0·19 grm. phosphate of lime.
10 grms. of commercial alizarine gave 1·18 grm. of ashes, of which
  0·003 grm. was soluble, and
  1·177 grm. insoluble. The latter contained
    0·814 grm. silica,
    0·256 grm. carbonate of lime, and
    1·103 grm. phosphate of lime.

10 grms. of madder-lake gave 1·20 grm. of ashes, of which
0·195 grm. was soluble, consisting of CaO, SO^3. The insoluble portion contained
0·450 grm. silica, and
0·550 grm. carbonate of lime with traces of phosphate.

Polytechn. Centralblatt, 1856, p. 292.

On Basaltic Glass. *By* C. Stickel.

The author recommends the employment of basalt in the manufacture of glass. The applicability of basalt to this purpose has long been known in the glass-houses, but the author gives some determinate proportions by which glasses of certain properties may be obtained:—

		drms.
1.	Powdered basalt	10
	Powdered white glass	10
	Soda	25
	Ashes	5

A very dark, brittle, ugly glass.

		drms.	grs.
2.	Basalt	10	0
	Minium	5	0
	Potashes	4	0
	White arsenic	0	5

Useless.

		drms.	grs.
3.	Basalt	10	0
	Quicklime	1	12
	Potashes	2	48
	Boracic acid	0	10

A nearly black, ugly, and very heavy glass, adapted for the decoration of monuments, stoves, &c.

		drms.	grs.
4.	Glass No. 1	5	0
	Peroxide of manganese	0	12

After strong fusion it forms fine, dark brownish-red, hard, glassy fragments, like Delft or Wedgwood's ware. It is adapted for plates, syrup-vessels, &c.

		drms.	grs.
5.	Basalt	5	0
	Broken glass	10	0
	Soda	10	0
	Ashes	5	0
	Peroxide of manganese	0	5

A beautiful light bottle-green glass, which is readily drawn into threads when fused. This was the most successful of all the experiments.—*Archiv der Pharm.*, lxxxv. p. 19.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Compounds of Arachic Acid.

By H. Scheven *and* A. Gössmann.

Arachate of Potash, $KO, C^{40}H^{39}O^{3}$.—Arachic acid was boiled with a concentrated solution of potash until the completion of the combination, which required several days' boiling. The mass, which contained an excess of potash, was evaporated to dryness by a gentle heat, and exposed in open dishes to the action of carbonic acid for a long time, to convert the greater part of the excess of caustic potash into carbonate, so as to render it insoluble in alcohol. The arachate of potash was then extracted from the powder thus obtained by alcohol of spec. grav. 0·815, and purified by repeated crystallization. If only a sufficient quantity of alcohol to effect the solution at a gentle heat be employed, the solution sets into a transparent jelly, which when dried upon bibulous paper falls into a light crystalline powder. With a larger quantity of alcohol the same compound separates after standing a longer or shorter time in more distinctly developed crystals.

0·405 grm. of the salt furnished 0·273 $KCl+PtCl_2$, representing 13·01 per cent. of potash; the amount, calculated from the formula of the neutral potash-salt, is 13·48. This neutral salt forms a clear solution in 15 to 20 parts of boiling water; but when this is diluted with 30 to 40 parts of water, the acid arachate of potash separates in shining laminæ.

Arachate of Soda, $NaO, C^{40}H^{39}O^{3}$, was prepared in the same way, and exhibited the same properties as the potash-salt.

Arachate of Ammonia, $NH^{4}O, C^{40}H^{39}O^{3}$.—A moderately concentrated alcoholic solution of arachic acid was saturated with an excess of ammonia, well covered, and set to cool gradually. An abundance of arachate of ammonia separated in distinct acicular crystals, which, when dried at the ordinary temperature, fell into a light, white crystalline powder. This neutral salt gives off ammonia when left in the air, even at ordinary temperatures; its analysis is therefore attended with difficulties, and as there could be no doubt as to the nature of the compound, it was not effected. When it was employed in the preparation of other salts, the authors made use of an alcoholic solution with a slight ammoniacal reaction.

Arachate of Magnesia, MgO, $C^{40}H^{39}O^{3}$.—An alcoholic solution of arachate of ammonia was mixed with a cold saturated solution of acetate of magnesia in excess, and the apparently amorphous precipitate thus produced was dissolved at a boiling heat. Neutral arachate of magnesia then separates in stellate prisms, first on the surface, and afterwards on the sides of the vessel. When purified by recrystallization and then dried, it forms a light, rather shining, white crystalline powder; it is difficult of solution in alcohol, and insoluble in water. The salt gave 6·27 per cent. MgO; the neutral salt ought to contain 6·19 per cent.

The preparation of a perfectly neutral magnesia-salt is attended with some difficulty. Thus if the above compound be washed longer than is necessary, or with hot alcohol, a basic compound remains on the filter, so that the amount of magnesia could be raised in the same compound to 8·6 and 9·24 per cent.; and a mixture of basic and neutral salts is obtained when a pure solution of arachic acid is mixed with an excess of acetate of magnesia. These peculiarities have already been observed in other higher members of this series of fatty acids; but in the case of arachic acid they are particularly remarkable, on account of the difficult solubility of their salts.

The compounds of arachic acid with the other alkaline earths were prepared in the same way as the magnesia-salt. They have a similar behaviour, but are more difficult of solution.

Arachate of Baryta, BaO, $C^{40}H^{39}O^{3}$, forms a light, white crystalline powder. It is soluble in large quantities of boiling alcohol, but insoluble in water. It gave 19·72 per cent. BaO; calculated for the neutral salt, 20·15 per cent.

Arachate of Strontia, SrO, $C^{40}H^{39}O^{3}$, is extremely similar to the baryta-salt, but is more readily soluble in boiling alcohol, and separates on cooling as a distinctly crystalline powder. It gave 14·0 per cent. SrO; calculated for the neutral salt, 14·6 per cent.

Arachate of Lime, CaO, $C^{40}H^{39}O^{3}$, forms a very loose, somewhat shining powder.

Arachate of Copper, CuO, $C^{40}H^{39}O^{3}$.—When an alcoholic solution of acetate of copper is mixed with a neutral solution of arachate of ammonia, a bluish-green precipitate is produced; this is amorphous at first, but gradually becomes crystalline by long standing, and consists of neutral arachate of copper. When dissolved in boiling alcohol and gradually cooled, it separates in distinct acicular crystals. When dried it forms a light, bluish-green crystalline powder, which melts at a high temperature. Its analysis gave—

	Found.		Calculated.
C^{40}	70·90	70·19	70·03
H^{39}	11·66	11·50	11·38
O^{3}	..	..	7·01
CuO	11·25	11·57	11·58

Arachate of Silver, AgO, $C^{40}H^{39}O^{3}$.—When prepared in the same way as the copper-salt, it forms at first an amorphous precipitate, which when dried by itself resembles chloride of silver in appearance, but only acquires a pale violet tint on exposure to the light. It dissolves pretty readily in boiling alcohol, and separates from this in white, somewhat shining prisms, which undergo no change by exposure to light. It furnished 26·94 and 27·28 per cent. AgO; calculated for the neutral salt, 27·70 per cent.

From this it appears that the salts of arachic acid approach those of the higher members of the fatty series; they possess, for the most part, the properties of the pure acid, being rather difficult of solution; so that they can often only be obtained in the form of a crystalline powder. In the preparation of the neutral salts, attention must be paid to the proper concentration of the solution and careful washing.

Arachate of Oxide of Æthyle, $C^{44}H^{44}O^{4} = C^{4}H^{5}O + C^{40}H^{39}O^{3}$.—Arachic acid is dissolved in absolute alcohol, and muriatic acid gas is passed into the slightly heated solution until saturation. The æther usually separates towards the end of the operation in the form of oleaginous drops upon the surface. Its formation is greatly facilitated by the digestion of the mixture. If the æther be then separated by mixing with water, and the whole operation be once repeated, the æther is generally so pure as not to require any treatment with carbonate of soda. Organic acids, especially acetic acid, also greatly favour the formation of the æther. It is owing principally to this circumstance, that there is always a considerable quantity of æther in the alcoholic mother-liquor of the fatty acid of the ground-nut oil, when, in employing the excellent process recommended by Heintz of partial precipitation with acetate of magnesia, the acetic acid set free is not neutralized from time to time with ammonia. Even by long boiling with alcohol, arachic acid is capable of forming its æther, a peculiarity which must be taken into account in purifying the acid by recrystallization. Hence it may easily happen, and the more so the stronger the alcohol employed and the longer the boiling, that the apparently purer acid may possess a lower melting-point than before. In such cases it is a mixture of æther and acid, as indicated by its higher amount of carbon.

Arachamide, $C^{40}H^{41}NO^{2}$.—Ground-nut oil was mixed with an excess of alcohol saturated with ammonia, well closed, and left for several weeks in a gentle heat with frequent shaking; it was then again saturated with ammoniacal gas, and as no further perceptible change took place for some time, the alcohol and excess of ammonia were removed by gentle heating with addition of water, the solid portions were collected on a filter after cooling, and freed from adherent oil, &c. by strong pressure. The residue thus obtained consisted principally of the amide of arachic acid, probably mixed with the amide of a lower member of the fatty acid series; it was repeatedly crystallized from alcohol. To get rid of all the intermixed ammoniacal salt, the alcoholic solution was agitated with a little free muriatic acid, and the amide again separated by water. When the melting-point no longer changed after crystallization, the substance was collected and analysed. The analysis gave—

C	77·09	77·07	..	..	40	= 240	77·17
H	13·18	13·09	13·07	..	41	41	13·18
N	..	..	..	4·27	1	14	4·50
O	..	..	..	..	2	16	5·14

It dissolves pretty readily in hot alcohol of spec. grav. 0·815, and separates abundantly on cooling in stellate prisms; it is insoluble in water, fuses at 208° to 210° F., and evolves no ammonia when solution of potash is poured over it, although it does so when fused with hydrate of potash.

Attempts to prepare the amide by heating the ammoniacal salt in a current of ammonia, by the action of the latter upon the æther at 140° F., and by enclosing alcohol saturated with ammonia in a glass tube, and heating it for several days in the water-bath, gave negative results. Arachic æther, sealed up in a glass tube with an alcoholic solution of ammonia, and heated for several days in the water-bath, and only opened after a contact of at least four weeks, was also unaltered.

Arachine was prepared by Berthelot's process. Equal parts of syrupous glycerine and arachic acid were sealed up in a glass tube. As no perceptible change took place by heating to 212° F. for several days, the temperature was gradually raised to 410° F., and this was maintained until the mass began to grow yellowish. The tube was cooled and opened, and the mass, which still contained an excess of glycerine, was repeatedly melted in hot water. The perfectly dry mass, which dissolved but sparingly in hot ordinary alcohol, was dissolved in a mixture of absolute alcohol and æther. Even in this it dissolved with difficulty, and quickly separated for the most part in the form of a flocculent, microscopically-crystalline mass. That portion alone which only separates by longer standing and the gradual evaporation of the solvent is distinctly crystalline.

The compound thus prepared is artificial arachine, and possesses the following properties:—It forms a colourless shining mass, resembling the natural neutral fats; it is very difficult of solution in alcohol of spec. grav. 0·833, but more readily soluble in absolute alcohol, and especially in æther; after its rapid separation from its hot ætherial or alcoholic solution, it forms a flocculent amorphous mass. When slowly separated, it is distinctly crystalline, consisting of interlaced needles; it fuses at 158° F., and when rapidly cooled exhibits an almost lustreless, non-crystalline fracture, whilst when slowly cooled it presents a distinctly crystalline structure. Its analyses gave—

C	76·22	76·20	
H	12·58	12·56	12·45

Berthelot has established a formula for the artificially prepared neutral fats, corresponding with the natural fats, which when applied to arachine agrees with the following proportions:—

$$3(C^{40}H^{40}O^{4})+C^{6}H^{8}O^{6}-6HO=C^{126}H^{122}O^{12}.$$

C^{126}	77·62
H^{122}	12·53
O^{12}	9·85

The results of the authors' analyses gave nearly $1\frac{1}{2}$ per cent. less carbon than required by Berthelot's formula. As the combustion was effected with oxide of copper and oxygen gas, an incomplete combustion could not have been the cause of this. The authors accordingly propose the following formula, as agreeing better with the results obtained:—

$$3(C^{40}H^{40}O^{4})+C^{6}H^{8}O^{6}-4HO=C^{126}H^{124}O^{14}.$$

C	76·22	76·20	..	126	=	756	76·21
H	12·54	12·56	12·54	124		124	12·50
O	..	..	..	14		112	11·29

Liebig's *Annalen*, March 1856, p. 257.

On the Loss of Silver by Cupellation.

By Burridge Hambly, F.G.S.*

The following experiments were made in the Metallurgical Laboratory of the School of Mines, Museum of Practical Geology, to ascertain whether the loss of silver by cupellation was the same when varying quantities were employed with a constant ratio of lead, and also to find the loss of silver when cupelled with a gradually increasing ratio of lead.

The metal employed in the experiments was purchased as fine silver, dissolved in nitric acid, precipitated as chloride, washed thoroughly, and reduced to the metallic state by fusion with carbonate of soda and charcoal.

Table I.

	Quantity of lead employed.	Quantity of silver employed.	Weight of silver globule obtained.	Calculated weight of silver in 1000 parts.	Loss of silver in 1000 parts.
	grs.	grs.	grs.		
In the muffle at the same time	250	25	24·738	989·5	10·5
	100	10	9·890	989·0	11·0
	10	1	0·988	988·0	12·0
In the muffle at the same time	250	25	24·720	988·8	11·2
	100	10	9·875	987·5	12·5
	10	1	0·987	987·0	13·0
In the muffle at the same time	250	25	24·746	989·8	10·2
	100	10	9·895	989·5	10·5
	10	1	0·988	988·0	12·0
In the muffle at the same time	250	25	24·730	989·2	10·8
	100	10	9·886	988·6	11·4
	10	1	0·988	988·0	12·0

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* Communicated by the Author.

The following are the mean of the foregoing results:—

Four cupellations, each made with 25 grs. of silver, gave a calculated loss in 1000 parts of	10·67
Four cupellations, each made with 10 grs., gave......	11·35
Four cupellations, each made with 1 gr., gave	12·25

TABLE II.

The weight of the silver employed in each of the following experiments was 5 grs.

Lead employed.	Ratio of lead to silver.	Per-centage of silver.	Silver obtained.	Calculated loss of silver in 1000 parts.
grs.			grs.	
5	1 to 1	50·0	4·973 4·972 4·972	5·5
15	3 to 1	25·0	4·954 4·954 4·957	9·0
25	5 to 1	16·16	4·942 4·946 4·946	11·1
35	7 to 1	12·5	4·940 4·941 4·942	11·8
45	9 to 1	10·0	4·933 4·932 4·933	13·4
50	10 to 1	9·09	4·926 4·922	15·2
75	15 to 1	6·25	4·919 4·920 4·918	16·2
100	20 to 1	4·76	4·916 4·916	16·8
125	25 to 1	3·84	4·912 4·912	17·6
175	35 to 1	2·77	4·904 4·910 4·904	18·8

From the experiments given in detail in Table I. the conclusion may, I think, be drawn, that according to the decrease in weight of the silver cupelled, so the loss of that metal very slightly increases, provided the ratio of lead employed be constant.

The experiments in Table II. tend to confirm the fact, already known, that an increasing ratio of lead produces an increasing loss of silver; but a far larger number of cupellations are requisite to determine with accuracy the extent and ratio of that loss.

On the Behaviour of Sulphuret of Mercury to the Compounds of the Alkaline Metals. By Dr. R. Weber.

When sulphuret of mercury is precipitated from a solution of a salt of that metal by means of an excess of sulphuret of ammonium, and a solution of hydrate of potash or soda is afterwards added, the precipitate is dissolved, and a colourless solution is obtained. If this be evaporated, a strong evolution of ammonia takes place, a crystalline film is formed at a certain degree of concentration, and on the cooling of the fluid crystals separate, which consist of chloride of potassium or sodium, when a solution of perchloride of mercury has been employed for the precipitation of the sulphuret. When these crystals are separated from the mother-liquor, and the latter is further concentrated by evaporation, a fresh crystalline film makes its appearance, and on cooling a dense mass of long, capillary, silky needles is formed. When the mother-liquor is separated by dropping through a funnel closed with a glass rod, and the needles are dried by pressing them between blotting-paper, the latter acquires an intensely black colour from the mother-liquor. By repeated pressure between fresh paper, the salt is at last obtained in the dry state and of a pure white colour.

The salt thus obtained has a strong alkaline reaction. When brought into contact with water it is immediately decomposed, black sulphuret of mercury being deposited, and the fluid separated therefrom contains free alkali as well as sulphuret of potassium.

The dry salt, heated in a test-tube, first of all gives off a large quantity of water; when more strongly heated it fuses, forming a red fluid, and globules of mercury are deposited on the cooler parts of the glass, but no vermilion is sublimed.

The salt dried between paper still contains a small quantity of chloride of potassium and chloride of ammonium; to get rid of these, it must be again dissolved in hydrate of potash, and the solution evaporated to crystallization. After the mother-liquor has been allowed to drain away, and the salt has been again dried by pressure between bibulous paper until the latter is no longer moistened, the salt must be carefully preserved from the influence of the atmospheric moisture, which it attracts with extraordinary avidity, deliquescing, and becoming decomposed with separation of black sulphuret of mercury.

The potash-salt, when recrystallized, consisted of—

HgS	=	46·28	1 atom.
KS		24·18	1 ...
KO		7·53	$\frac{2}{3}$ ...
HO		22·01	6 ...

The purified salt, prepared with hydrate of soda, consists of—

HgS	=	47·70	1 atom.
NaS		16·08	1 ...
NaO		7·37	$\frac{1}{2}$ ...
HO		28·85	8 ...

Sulphuret of mercury therefore forms a sulpho-salt with the protosulphurets of potassium and sodium; but this can only exist either in solution or in the solid form in the presence of free alkali. Any attempt to extract the free alkali from the salt causes its immediate decomposition into black sulphuret of mercury, which is deposited, and sulphuret of potassium or sodium, which remains in solution.

The quantity of free alkali stands in no determinate proportion to that of the sulpho-salt. The salt can only be obtained in the dry state by pressure between paper, and the amount of free alkali extracted by this process is variable, but it is impossible to remove all the free alkali in this manner. If the pressure between paper be very long continued, even this produces a decomposition of the salt with separation of black sulphuret of mercury.

The white sulpho-salt crystallized in needles dissolves in a very small quantity of hydrate of potash, and the solution may then be diluted with water without undergoing any change. But if the quantity of water added be increased, it produces too great a dilution of the free alkali present, without which the sulpho-salt cannot exist, and the fluid acquires a black colour from the separation of sulphuret of mercury. The action of alcohol is exactly similar.

When the salt is dissolved in a small quantity of hydrate of potash and the solution diluted with a little water, it exhibits the following phænomena:—Sulphuretted hydrogen or sulphuret of ammonium immediately produces a precipitate of sulphuret of mercury. The same effect follows the addition of a little powdered sulphur to the solution with the application of a gentle heat. In these cases the free alkali is converted into sulphuret; and as soon as this is present in excess, the decomposition of the salt, with separation of black sulphuret of mercury, takes place. The solution of the sulpho-salt may also be mixed with solutions of any neutral alkaline salts without undergoing any change; but if these be added in very great excess, they act as diluents upon the free alkali, and thus induce the decomposition. If the concentrated solution of the sulpho-salt be mixed with a solution of biborate of soda, or one of an alkaline bicarbonate, or of the ordinary phosphate of soda, $(NaO)^2 HO, PO^5+24HO$, black sulphuret of mercury is immediately thrown down.

The sulpho-salt can also be obtained in a different manner from the one above given. If a solution of perchloride of mercury be precipitated by a current of sulphuretted hydrogen, and the sulphuret of mercury, after separation from the acid fluid and washing with water, be suspended in a solution of hydrate of potash or soda by constantly stirring, whilst a current of sulphuretted hydrogen gas is passed through the mixture, it is soon completely dissolved. As soon as the solution has taken place, the passage of the sulphuretted hydrogen must be stopped, for when the free alkali begins to be saturated with it, the whole of the sulphuret of mercury is again separated. This is one of the most distinct proofs that the sulpho-salt can only exist in the presence of free alkali. If the solution be evaporated, the salt is obtained crystallized in white needles.

It is also formed when red or black sulphuret of mercury is mixed with about the same quantity of sulphur that is contained in it in a porcelain crucible, and then fused with an excess of solid hydrate of potash. When the cold mass is treated with water, a perfectly clear solution is obtained, which may also be brought to crystallize by evaporation.

It is therefore only the protosulphurets of potassium and sodium that are capable of forming a sulpho-salt with sulphuret of mercury in the presence of free alkali.

Twenty-six years ago Brunner observed the formation of the same salt in the preparation of red sulphuret of mercury in the humid way, when it was prepared according to Kirchhoff's prescription from 300 parts of mercury, 68 parts of sulphur, and 160 parts of potash. Brunner states that in these proportions the quantity of alkali is too great, and gives rise to the formation of this sulpho-salt. The amount of vermilion obtained is in consequence very small, as a considerable quantity of sulphuret of mercury is retained in solution by the sulphuret of potassium formed. According to Brunner, the salt consists only of $KS + HgS + 5HO$. He also endeavoured, but unsuccessfully, to prepare this compound in another way, by treating vermilion with hyposulphite of potash and sulphuret of potassium.—*Ber. der Akad. der Wiss. zu Berlin*, 1856, p. 9.

On the Composition of Fulminating Silver. By O. B. KÜHN.

After an introduction, in which the author treats of isomerism, metamerism, mono- and bibasic acids, and afterwards particularly of the views entertained respecting the salts of cyanic, cyanuric and fulminic acids, he again maintains the assertion long since made by him with regard to fulminating silver, namely, that the composition of this body is $AgCy + AgO + CyO^3$. Although a cyanic acid with 3 atoms of oxygen has not yet been isolated, this may be explained by its great decomposability, which is manifested in the explosive properties of its compounds. The author has endeavoured to study this decomposability, and the presence of more oxygen than is contained in cyanic, acid by the action of the fulminates upon oxidizable bodies; ferrocyanide of potassium appeared to him to be a proper substance for the manifestation of such actions.

The experiments were as follows:—A weighed quantity (0·857) of fulminating silver dried over sulphuric acid, which had not the least acid reaction, and when decomposed by muriatic acid showed exactly the amount of silver determined by Gay-Lussac and Liebig (72·0 per cent.), was treated with boiling water, and a normal solution of ferrocyanide of potassium was added to it in small portions, so that the quantity of the salt required for the decomposition of the fulminating mercury was divided into fourteen not quite equal parts. The vessel was placed for about ten minutes in boiling water after each addition. The following observations were made:—

1st Portion.—The fluid acquired a slight bluish colour; the white fulminating silver became brownish; the bluish colour of the fluid disappeared on the application of heat.

2nd Portion.—The blue colour was considerable, but disappeared quickly on the water-bath; thick white flakes, easily distinguishable from the brownish mass, were formed; the fluid was rendered very turbid by nitric acid.

3rd Portion.—The strong blue colour of the fluid quickly disappeared on the water-bath; the sediment became darker.

4th Portion.—As before, but the blue colour remained longer.

5th Portion.—A blue coloration, which however soon passed to red, before the flask was put into the water-bath; it could be well held in the hand, and was therefore about 86° F.; the sediment also appeared bluish, and after heating greenish-blue; the fluid reddish, like a weak solution of cobalt. At this period, 0·595 of ferrocyanide of potassium had been employed, and therefore to 1 equiv. of fulminating silver (=300·2) 208·4, or not 1 equiv.

6th Portion.—The fluid lost its colour before exposure to the water-bath, but when heated it again became blue, and afterwards behaved as No. 5; the fluid contained neither ferridcyanide of potassium nor nitroprusside of potassium.

7th Portion.—As before, but the red colour of the fluid is stronger, furnishing the first distinct indication of ferridcyanide of potassium; 0·682 of ferrocyanide of potassium had now been employed, or rather more than 1 equiv. to 1 equiv. of fulminating silver (0·857 : 0·682=300·2 : 239·0, instead of 211·4).

8th Portion.—The fluid became paler, but acquired a darker colour on the water-bath; the sediment was ash-gray.

9th Portion.—As before; in particular places, where a little fulminating silver had been deposited at the commencement, there was a yellowish-brown colour.

10th, 11th and 12th Portions.—No change, but the sediment had a tinge of brown.

13th Portion.—Sediment distinctly brown and flocculent; the fluid showed no reaction of sesquichloride of iron.

14th Portion.—Sediment like oxide of iron; the fluid exhibited the reactions of protochloride of iron, and also of the sesquichloride. 1·277 of ferrocyanide of potassium had now been employed, or rather more than 2 equivs. (0·857 : 1·277=300·2 : 447·3 instead of 422·8). The residue was filtered off, and when heated to redness left 0·210, which was dissolved in nitric acid; from this, 0·194 of chloride of silver (=0·146 metallic silver) and 0·064 of sesquioxide of iron were obtained.

In a second experiment, 1·176 of ferrocyanide of potassium were employed with 0·827 of fulminating silver, before the point was attained (0·827 : 1·176=300·2 : 426·9). The insoluble residue when calcined amounted to 0·167, and the silver contained in it to 0·0851. This residue, and the amount of silver or cyanide of silver contained in it, are therefore dependent upon particular circumstances, for in the first experiment the silver in the residue amounted to between one-fourth and one-fifth, in the second to about one-seventh.

The dark red fluid gives the following reactions:—With nitric acid a dark olive-coloured precipitate is produced, which soon becomes yellowish-brown, and in two hours rust-coloured; much hydrocyanogen is evolved.

Sulphuric acid produces a similar precipitate, which changes in the same manner, and much hydrocyanogen is evolved. The filtered fluid is of an amethyst colour, and becomes blue with protochloride of iron, but not with sesquichloride.

Acetic acid gives a dirty white precipitate, which acquires a blue colour in the air; the red filtrate remains long unchanged in the air, but acquires a deep grayish-black colour with sulphuretted hydrogen, and gives a precipitate of the same colour.

Muriatic acid produces a copious white precipitate, and the filtrate is pale red.

With nitrate of silver, as with sesquiferrocyanide of potassium, a precipitate is produced which does not explode, but which changes in time, becoming white on the surface.

Sulphate of copper furnishes a similar precipitate; the blue filtrate gives with nitric acid, a white precipitate, which does not explode.

Sulphate of zinc gives a dingy reddish-brown precipitate; the filtrate is pale rose-red, but loses its colour in sixteen hours.

Protochloride of iron produces a dark blue precipitate, not quite so dark as Turnbull's blue, because the solution of the reagent contains a little free muriatic acid, and therefore throws down a small quantity of chloride of silver; in the filtrate, nitric acid produces a strong white precipitate, which does not explode, and which acquires a slight tinge of blue when washed.

Nitrate of baryta produces a slight turbidity, and the fluid becomes paler than by dilution to an equal degree. The colour does not disappear in two days.

Solution of caustic potash produces no change in the cold; when boiled it destroys the colour, without producing any remarkable odour; there is particularly no ammoniacal smell; a body resembling peroxide of iron, especially that obtained from the so-called nitroprusside of potassium, is separated; the fluid resembles a solution of nitroprusside of potassium in colour; but the precipitate from the latter is brown, whereas in the present case it is red. The reaction with an alcoholic solution of sulphuret of potassium cannot be produced in any way. The beautiful red fluid, freed from silver by muriatic acid, loses its colour with great rapidity when treated with hydrosulphate of ammonia; with pure nitroprusside of potassium a dark blue colour is first produced, and afterwards a black precipitate.

From these experiments the author concludes that the fulminating silver has produced a partial oxidation of the ferrocyanide of potassium. And although it cannot yet be determined what body is produced together with the ferridcyanide of potassium and the cyanide of silver and potassium, to cause the red colour of the fluid, it is clear that the above-mentioned phænomena cannot be explained from the bibasic condition of fulminic acid, as they differ essentially from those produced by cyanate and cyanurate of silver.

The author has instituted two series of experiments parallel with the above, with both the silver-salts just mentioned. The results showed that these salts differed from fulminate of silver in their behaviour towards the ferrocyanide of potassium, as they produced no oxidation of that body, and behaved in general like other insoluble or sparingly soluble silver-salts.

At the conclusion of his memoir, the author opposes the objections raised by Berzelius against his adoption of a tritoxide of cyanogen, and also the view put forward by Berzelius, that the explosive properties of fulminating silver might be due to a metallic nitruret contained in it. He also contraverts the opinion expressed by Gerhardt and Laurent, that hyponitrous acid may be contained in fulminating silver, ($C^4 N (NO^4) Ag^2$=fulminating silver.—*Central Blatt.* No. 39, 1855.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Theoretical and Practical Investigation on the Fixation of Colours in Dyeing. By F. KUHLMANN. (Part I.)

IT was generally supposed by those chemists who first occupied themselves with the complicated phænomena of the art of dyeing, that azotized materials possess the greatest aptitude for the reception of dyes. In support of this, they instanced the greater ease with which silk and wool were dyed in comparison with cotton and linen. In the red dyeing of Adrianople, it was considered that the employment of baths of sheep's dung must give a sort of animalization to the cotton, and baths of cow-dung might be considered by dyers as producing a similar result. These notions, as regards cow-dung, have been abandoned by chemists, especially as several saline substances, particularly silicate of soda, have been substituted for it as a means of fixing the mordants.

M. Chevreul has shown that the more or less easy fixation of colours upon tissues depends sometimes upon the nature of the latter, and sometimes upon that of the colouring matter itself. The author has tried whether cotton modified by combination with the elements of nitric acid, or by transformation into pyroxyline, would acquire a peculiar disposition for absorbing colouring matters. He carefully prepared a quantity of pyroxyline with cotton and linen tissues; and also with cotton-wool; operating by Meynier's process with a mixture of monohydrated nitric acid and concentrated sulphuric acid. The pyroxyline was washed several times with a large quantity of water, soaked for some time in a solution of crystallized carbonate of soda, and washed again. The pyroxylized tissues were prepared for dyeing by the following treatment:—They were soaked for twenty-four hours in cold water, pressed and rinsed, then soaked in boiling water, and after a fresh washing they were half-dried and calendered for printing.

Various mordants were printed simultaneously upon pyroxylized linen and cotton tissues, and upon portions of the same in their natural state, the latter having been completely freed from foreign matters by boiling for three hours in a weak solution of carbonate of soda, then washed and treated with a bath slightly acidulated with sulphuric acid, and after being washed again and half-dried, calendered to prepare them for printing.

The azotized and non-azotized tissues were printed at the same time with the following mordants:—

Black	Pyrolignite of iron of 7° Baumé. Thickened with starch.
Puce	2 parts of pyrolignite of iron of 10°. 1 part of pyrolignite of alumina of 8°. Thickened with starch.
Red.........	Pyrolignite of alumina of 8°. Thickened with soluble starch.
Violet	Pyrolignite of iron of 1°. Thickened with soluble starch.
Lilac	Pyrolignite of iron of ½°. Thickened with soluble starch.
Brown	Decoction of catechu with acetic acid. A little nitrate of copper.

After impression, the tissues were suspended for six days in the cold, and one day in the hot oxidizing chamber. They were freed from gum in a bath of cow-dung and chalk of 158° F. for ten minutes, well cleaned, treated a second time in the same bath at the same temperature, cleaned and rinsed. The dyeing was effected with garancine in a bath of river-water slightly acidulated, commencing with a temperature of 95° F., and rising gradually in three hours to 185° F.; lastly, the tissues were pressed, rinsed, and dried. The dyed samples were halved, and one-half of each bleached with chloride of lime.

These operations proved the following facts:—All the azotized tissues remained excessively pale compared with the non-azotized ones, notwithstanding the superabundance of the colouring matter. The azotized tissue, although it rejects the mordants, appears to possess the power of combining, without their aid, with a portion of the colouring matter of madder, to judge from the yellowish tint which remains even after the treatment with chloride of lime.

To ascertain whether these results were due to exceptional causes, especially to a portion of acid which might have escaped the washings, the author repeated his experiments, soaking the azotized tissues for twenty-four hours in a weak tepid bath of crystallized carbonate of soda, rinsing them, and washing them repeatedly. They were then calendered, moistened, and printed after drying. After immersion in the mordants, they were suspended in the fixing chamber for eight days. They were freed from gum, and dried in the same way as in the preceding experiment, when exactly the same results were obtained.

Other pieces of cotton, and one of linen, were heated with a hot-bath of pyrolignite of iron, and then passed into a bath of nut-galls. The azotized tissues acquired a very pale tint compared with those in their natural state.

Dyeing with prussian blue was then tried upon cotton-wool. As in the black-dyeing with gall-nuts, the pyroxylized cotton only acquired a very pale tint compared with that in the natural state. The same results were obtained in a series of experiments with cotton-wool, in which Brazil-wood was substituted for garancine.

M. Béchamp's recent experiments having shown the possibility of reducing pyroxylized cotton to its original state, the author wished to ascertain whether in this case it also regained its capacity for dyeing; he found that pyroxyline, treated by Béchamp's process, recovered ~~its property~~ of receiving colours.

The author had retained a considerable quantity of pyroxylized cotton tissues. These were rolled up tightly, and kept in a wide-mouthed bottle closed with a cork. In about two months he observed that the bottle was filled with nitrous vapours, and that the cork, which was corroded by nitric acid, had been raised to give passage to the reddish vapours. The author was unable to ascertain the cause of this spontaneous decomposition, for some pyroxylized cotton which had been dyed and preserved for the same period had undergone no alteration. He washed the decomposed pyroxyline, but its texture was greatly changed, and tore with a slight touch, and its inflammability was considerably diminished.

The results of its analysis, as confirmed by M. Wurtz, were as follows:—The substance was dried *in vacuo* at 212° and 230° F.

C	31·25
H	4·08
N	7·88

The analyses of gun-cotton give—

	Demonte and Menard.	Béchamp.	
C	28·5	28·5	27·9
H	3·5	3·5	3·5
N	11·6	10·5	11·1

The comparison of these results shows that pyroxylized cotton after this spontaneous decomposition contains two-thirds less nitric acid than unaltered gun-cotton.

This partially denitrified pyroxyline was dyed with garancine and Brazil wood after mordanting with acetate of alumina, when the author was astonished to find, not only that it no longer rejected the colouring matter like pyroxylized cotton, but that it furnished infinitely stronger and brighter colours than non-azotized cotton treated in the same way. Thus with Brazil wood and a mordant of acetate of alumina a tint approaching scarlet was obtained, and this induced the author at once to attempt the production of a nitrated cotton with the same power of fixing colours possessed by that which he had obtained by accident. After ascertaining unmistakeably that the nitrous elements retained in this were in chemical combination with the cellulose, he soon perceived that these elements had not entered into such a stable state of combination, in the presence of salts of protoxide of iron, as that in which they exist in pyroxyline.

Decomposed pyroxyline and ordinary pyroxyline were exposed to a gentle heat in a bath of protosulphate of iron. In a very short time the altered pyroxyline acquired a chamois-yellow colour, whilst the pyroxyline took up much less oxide of iron than ordinary cotton under the same circumstances. The same differences of colour were reproduced when the oxide of iron was converted into prussian blue by a slightly acidulated bath of ferrocyanide of potassium. Thus pyroxyline, by losing a portion of its nitrous elements, not only loses its resistance to the absorption of mordants and colours, but actually becomes far more capable of becoming charged with these bodies than non-azotized cotton.—*Comptes Rendus*, April 14, 1856, p. 673.

On the Purification of Amorphous Phosphorus. By E. NICKLÈS.

Amorphous phosphorus, incapable of spontaneous inflammation, is obtained by keeping ordinary phosphorus for some time at a temperature of between 446° and 482° F. in an inert atmosphere; but however long the treatment may be continued, there is always a portion of the phosphorus which escapes the transformation, and which must afterwards be got rid of completely in order to avoid destroying the essential properties of amorphous phosphorus.

The disadvantages of the mode of purification proposed by Schrœtter have long been recognized; it is founded on the solvent action of sulphuret of carbon upon ordinary phosphorus, whilst it has no action upon the red variety. The operation therefore seems very simple, but in practice it is attended with much inconvenience and danger; the washings are interminable, and the chances of inflammation increase rapidly with the quantity of phosphorus under treatment. To avoid this danger, Schrœtter recommends that the filter on which the washing is carried on should be kept constantly full of sulphuret of carbon, to prevent the ordinary phosphorus, which is deposited in a very finely divided state upon the edges of the filter, from causing the inflammation of the whole; but even this precaution is not sufficient to avoid accidents.

The author tried several methods of effecting the separation of the ordinary phosphorus by chemical means, but without success, and he has accordingly availed himself of the different densities of the two bodies to effect his purpose, by agitating them with a fluid of specific gravity intermediate between them. Amorphous phosphorus has a specific gravity of 2·106, and ordinary phosphorus of 1·77; a solution of chloride of calcium of 38° to 40° B. will serve for their separation; the ordinary phosphorus being lightest, floats on the surface, when it may be easily taken up by a little sulphuret of carbon, and the operation may be carried on in a closed vessel.

The process is as follows:—A little sulphuret of carbon is put into the retort in which the conversion has been effected; if the substance, which usually adheres strongly, is not detached, the bottom of the retort is dipped into luke-warm water, when the disaggregation of the substance takes place immediately with a slight noise. When the phosphorus is detached, the saline solution is added, the vessel is closed and shaken, and the sulphuret of carbon containing the ordinary phosphorus floats on the surface. If the proportion of the latter is not more than one-fourth, it may be completely got rid of by a single washing, but it is safer to decant the phosphorized sulphuret of carbon and replace it by a fresh quantity of pure sulphuret. This is necessary when the two forms are mixed in equal proportions, but the author says that three washings are always sufficient to remove every trace of ordinary phosphorus.

After separating the two liquids by decantation, the saline solution containing the amorphous phosphorus is poured upon a cloth, when the purity of the product is so perfect that there is no occasion to boil it with a solution of caustic potash. The whole operation may be completed in half an hour and without the least danger, so that it may be carried on even by inexperienced hands, which is of no small importance now that red phosphorus is an article of commerce.—*Comptes Rendus*, April 7, 1856, p. 646.

PROCEEDINGS OF SOCIETIES.

Royal Society.

April 17, 1856. (The Lord Wrottesley, President, in the Chair.)

"On the Condition of the Oxygen absorbed into the Blood during Respiration." By George Harley, M.D.

The author commences by explaining, that his researches were instituted with the view of ascertaining whether the doctrine maintained by Magnus in regard to the gases interchanged in the lungs during respiration were correct—namely, that the gases in question enter into *no* chemical combination with the constituents of the blood, either in passing to or from the tissues and organs of the body, but form merely a physical mixture with the circulating liquid. The principal object of the inquiry was to determine the following points:—

1. Has blood the property of chemically combining with the respired oxygen?
2. Which of the constituents of the blood enter into combination with oxygen?
3. Do these constituents, by combining with oxygen, simply become oxidized, or do they also yield carbonic acid gas?
4. What are the agents which control these changes?

After describing the method of investigation, and the apparatus employed, the author proceeds to relate a few of the analyses which he considered as the most conclusive. Instead of confirming the view of Magnus, that gases enter into no chemical combination with blood, his results led him to conclusions of an opposite character, which serve to confirm the more generally received doctrine.

In one set of experiments a certain quantity of fresh ox-blood was first shaken with renewed portions of air until it had become thoroughly saturated with oxygen, then introduced into a graduated glass vessel with 100 per cent. of ordinary air, corked carefully up, and kept during twenty-four hours in a room of moderate temperature. In order to favour the mutual action of the air and blood, the vessel was frequently agitated. At the expiration of twenty-four hours the gas was analysed by Bunsen's method. In an example cited the following was found to be its composition :—

Oxygen..........	10·42	total oxygen.. 15·47
Carbonic acid	5·05	
Nitrogen	84·53	
	100·00	

On comparing this with the composition of the common air (oxygen 20·96 ; carbonic acid 00·002 ; nitrogen 79·038) which had been introduced into the vessel, it is seen that 10·54 per cent. of oxygen has disappeared, while 5·05 per cent. of carbonic acid now exists, where only a trace of its presence could before be detected.

Similar results were obtained with defibrinated blood. In a case where defibrinated arterial blood from a calf, after complete saturation with oxygen, was kept in contact with an equal volume of air during twenty-four hours, and treated exactly as in the previous example, the gas on analysis yielded in 100 parts,—

Oxygen..........	11·33	total oxygen=17·29
Carbonic acid	5·96	
Nitrogen	82·71	
	100·00	

showing in this case also that the air which had been imprisoned during twenty-four hours along with blood, no longer possessed its original composition, but that some of its constituents had been materially increased, while others had diminished in a manner no less marked.

It would appear from these examples that the blood had probably become oxidized in two ways; first, by giving off a quantity of carbon, and secondly by directly combining with oxygen. As to the portion of oxygen which has disappeared, and which is not accounted for by the carbonic acid evolved, it may have combined partly with another portion of carbon, to form a limited amount of carbonic acid, which by the law of absorption is retained in the blood; and partly with hydrogen or some other oxidable constituent of the blood, without yielding a gaseous product.

These two experiments it will be observed point to exactly the same conclusions, and together with a number of others, where the mode of procedure was similar, and which were attended with similar results, have satisfied the author as to the fallacy of Magnus's doctrine, "that the oxygen received during respiration into the blood is kept there merely by the law of mechanical absorption, and enters into no chemical combination with that liquid." Had this assertion been well-founded, such a change as has been seen to occur, in the composition of the air enclosed along with blood, saturated as the blood already was with oxygen, could not have happened.

After having ascertained that air underwent certain changes in composition during its contact with blood, it next became an object to discover by which of the constituents of the blood these changes were induced. With this view the author successively subjected the organic compounds of the blood separately to the action of air, by a similar process to that adopted in the case of the blood itself.

A certain quantity of fresh fibrine, moistened with water, was saturated with oxygen, placed in a receiver along with eight volumes of air, and kept during twenty-four hours at a temperature of from 20° to 25° Cent. At the expiration of this time the gas on analysis was found to have the following composition:—

Oxygen	6·81	total oxygen.. 17·98
Carbonic acid	11·17	
Nitrogen	82·02	
	100·00	

thus showing that fibrine takes up a certain quantity of oxygen, and gives off a stated amount of carbon combined with oxygen in form of carbonic acid gas.

The next experiments were made upon albumen, but as that substance could not be obtained in a pure, and at the same time uncoagulated state from blood, the albumen of the hen's egg was employed, which possesses very similar characters. It was found that when a certain quantity of the white of the hen's egg was well saturated with oxygen, and afterwards kept in contact with an equal volume of air during a certain number of hours at a temperature of 36° Cent., the gas on analysis gave in 100 parts,—

Oxygen	17·05
Carbonic acid	2·09
Nitrogen	80·86
	100·00

proving, in common with the experiments on the blood and on fibrine, that albumen also possesses the property of absorbing oxygen and disengaging carbonic acid.

Some comparative experiments were also made upon serum and upon blood-coagulum, in which it was found that the air confined along with the serum yielded on analysis—

Oxygen	16·74
Carbonic acid	2·30
Nitrogen	80·96
	100·00

while that confined with the coagulum contained—

Oxygen	8·57
Carbonic acid	7·29
Nitrogen	84·14
	100·00

It thus appears that the oxygen exerted a much more powerful action on the coagulum, which contained the fibrine and blood-corpuscles, than on the serum, which contained only albumen. The experiment thus corroborated the results previously obtained with pure fibrine and pure albumen. The pure fibrine was seen to produce a much greater change in the composition of the atmospheric air than the pure albumen from the hen's egg. The difference in the case of the coagulum and the serum was so much marked, that the author felt anxious to find out whence it proceeded; and under the impression that the hæmatin in the corpuscles might have mainly contributed to the result (as other organic colouring matters possess the property of absorbing oxygen and giving off carbonic acid gas), he took a small quantity of pure blood-hæmatin prepared by Verdeil's process, and put it into a vessel along with 1000 volumes of ordinary air. After the air had been kept in contact with the hæmatin for some months, the gas was analysed and found to contain—

Oxygen	16·01
Carbonic acid	3·80
Nitrogen	80·19
	100·00

The pure colouring principle of the blood, therefore, by exposure to ordinary air, gives off carbonic acid gas, and becomes oxidized in two ways; first by a loss of carbon, and secondly by direct combination with oxygen. The author considers that this last result furnishes additional evidence of the correctness of an opinion he hazarded two years ago*, imputing to the colouring matters of the vegetable and animal economy a more important office in the function of respiration than they before had been considered to possess, and regarding their principal function in organized beings as the absorbing of oxygen and exhaling of carbonic acid—a view altogether irrespective of Liebig's well-known hypothesis, which assigns the above office to the iron of the blood-hæmatin.

The author concludes by expressing the hope that his experiments will be considered as at least serving to establish one important fact respecting which further evidence was wanted, namely, that the entire volume of the respired oxygen is not transmitted in an uncombined state (as Magnus believes) to the various organs and tissues of the body, but that a portion of it enters into chemical combination with some of the organic constituents of the blood.

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* Verhand. Physik-Medizin. Gesellsch. zu Würzburg, Bd. v. 1854; and Erdmann's Journ. f. prakt. Chemie, Bd. lxiv. H. 5. 1855.

PATENT.

Patent granted to C. Tennant Dunlop, *for Improvements in the Manufacture of Chlorine.*

This invention relates to the employment of the residuum obtained in the manufacture of chlorine, which residuum ordinarily consists of chloride of manganese, in the preparation of an artificial oxide of manganese, which is well suited for the manufacture or production of chlorine. The special process preferred by the patentee in carrying out his invention is the transformation of the chloride of manganese into a carbonate of manganese by the agency of any of the means already well known to chemists, and then subjecting the carbonate thus prepared to the action of heat in contact with atmospheric air. Whatever impurity the chloride of manganese may contain, as chloride of iron for instance, is first separated either by calcination or by the agency of a suitable precipitant. Practical working has decided that the carbonate of manganese, thus treated, yields an oxide of manganese of a richness equivalent to about 80 per cent. of pure peroxide.

The carbonate of manganese may be obtained by precipitation from the chloride of manganese by the agency of carbonate of ammonia. The muriate of ammonia resulting from this treatment may either be sold or employed as such, or it may be retransformed into a carbonate in the usual way, and then again employed for the precipitation of fresh chloride of manganese. Hydrate of lime is also employed in the production of carbonate of manganese from these residual matters; the hydrated oxide of manganese thus obtained being subsequently transformed into carbonate of manganese by the transmission through it of carbonic acid.

By another process, carbonate of manganese is obtained by passing carbonic acid through the solution of chloride of manganese which has been previously mixed with a quantity of carbonate of lime. The carbonate of lime, under the influence of the carbonic acid, decomposes the chloride of manganese into carbonate of manganese, from which latter substance the oxide of manganese can be obtained, as well as chloride of calcium, which remains in solution. The production of oxide of manganese suitable for the obtainment of chlorine has been often attempted by following the process of precipitating the manganese as an oxide, and then bringing it to a higher state of oxidation by heating it in contact with atmospheric air, as well as by other means. But the essential feature of the present invention is, the production of oxide of manganese from the residuum of the chlorine manufacture, by first manufacturing or producing the carbonate of manganese, and then heating this carbonate in contact with atmospheric air.—Dated May 31, 1855.

THE CHEMICAL GAZETTE.

No. CCCXXVII.—June 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Concentrated Sulphuric Acid upon Ferrocyanide of Potassium. By C. GRIMM *and* G. RAMDOHR.

ACCORDING to Fownes*, when 1 part of finely powdered ferrocyanide of potassium is heated with 9 parts of concentrated sulphuric acid, very pure carbonic oxide gas is obtained, which only contains a small quantity of sulphurous acid towards the end of the operation, but never any trace of carbonic acid. In several experiments, however, we found that the carbonic oxide gas obtained by this process always contained a small proportion of carbonic acid besides the sulphurous acid. As this mode of preparing carbonic oxide gas had hitherto not been generally adopted, it appeared to us to be interesting to submit it to a repeated trial, and especially to submit the carbonic oxide gas thus obtained to an exact eudiometric examination.

We observed the occurrence of carbonic acid only at the commencement of the operation, simultaneously with that of the sulphurous acid. The evolution of both these gases soon ceases, and then chemically pure carbonic oxide gas is obtained. When the mixture of sulphuric acid and ferrocyanide of potassium is heated to a certain degree, which may easily be recognized by the commencement of frothing in the flask, the evolution of the carbonic oxide gas goes on for a considerable time by itself, so that it is the best plan to heat it very carefully, and to cease the application of heat as soon as this point is attained. When the spontaneous evolution of gas ceases, if heat be again applied, a further portion of carbonic oxide is obtained, but this is more or less contaminated with sulphurous acid. At first a white mass is produced in the flask, which is similar in appearance to the compound of protocyanide of iron and cyanide of potassium ($KCy+2FeCy$), which remains after distillation in the action of dilute sulphuric acid upon ferrocyanide of potassium mixed with sulphate of potash. In the course of the operation this dissolves completely, and the solution only becomes turbid at the close, with an abundant deposition of small, white, nacreous, laminar crystals. These may easily be obtained from the residue, by diluting the mass with water and separating the fluid from the crystals by filtration. If the mixture be not heated long enough, these crystals are not obtained by mixing with water, but prussian blue is separated and sulphate of potash dissolved in the fluid:—

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* Chem. Gaz., vol. i. p. 442.

I. *Analysis of the Gas.*

	Volume observed.	Temperature Fahrenheit.	Barometer.	Height of the column of mercury above the trough.	Corresponding volume at 32° F. and 1000 mill. pressure.	
1. Original volume (moist).........	126·1	38·48	729·1	52·9	83·1	Difference = 9·8 CO^2 and SO^2.
2. After absorption of CO^2 and SO^2 (dry)	112·4	38·84	728·6	66·8	73·3	
3. Volume of gas after transfer (moist).........	245·0	39·05	730·1	421·6	73·0	Difference = 90·4 vols. O.
4. After admission of oxygen (moist).........	379·5	39·56	730·4	287·0	163·4	
5. After combustion (moist)...	331·7	39·92	730·8	334·5	127·3	Difference = 73·6 vols. CO^2.
6. After absorption of CO^2 (dry)	202·8	40·64	733·7	464·2	53·7	
7. After admission of hydrogen (dry)	515·4	41·36	733·1	152·7	293·5	Difference = $\frac{161·7}{3}$ = 53·9 vols. O.
8. After combustion (moist)...	338·4	41·36	731·5	328·0	131·8	

The difference between 1 and 2 (9·8) gives a per-centage amount of 11·79 in carbonic and sulphurous acids. On the other hand, it is clear that 73·0 of the gas freed from CO^2 and SO^2 formed 73·6 vols. CO^2 (difference between 5 and 6). Consequently 90·4—53·9=36·5 vols. of oxygen were required. The missing 53·9 vols. of oxygen are found from the difference between 7 and 8$=\frac{161·7}{3}=$53·9. As 36·5 vols. of oxygen are required for the combustion of 73·0 vols. CO into CO^2, it follows that the gas freed from CO^2 and SO^2 consisted of chemically pure carbonic oxide. 100 vols. of the gas examined therefore consisted of 11·79 CO^2 and SO^2, and 88·21 CO.

II. *Analysis of the Laminar Crystals.*

After the completion of the action of sulphuric acid upon ferrocyanide of potassium, which is recognized by the cessation of the evolution of SO^2, the entire mass was diluted with water, and the crystals were collected on a filter and washed. During the washing the crystals acquired a violet tinge; when dried, they appeared slightly yellowish, with a nacreous lustre, very similar to sulphate of aniline. They were dried by keeping them for a few days over ordinary sulphuric acid, and then heated for a considerable time to 212° F. in the air-bath. Their analysis gave—

Oxide of iron	30·10
Sulphuric acid	61·70
Potash	8·54

These numbers represent no determinate equivalent proportion, as the formula $2(Fe^2O^3, 3SO^3)$ KO, SO^3 requires—

Oxide of iron	32·8
Sulphuric acid	57·4
Potash	9·6

In washing the salt, we noticed that the water had an acid reaction even after long washing, so that it produces a partial decomposition of the salt, which may explain the difference between the numbers found and calculated. The solution separated from the crystals after the completion of the action of sulphuric acid upon ferrocyanide of potassium contains potash and ammonia together with sulphuric acid.

From the above results it appears that this method of preparing carbonic oxide gas, notwithstanding the occurrence of carbonic acid and sulphurous acid, is still useful. In this convenient and cheap way an abundant supply of carbonic oxide gas may be obtained, by taking the precaution of purifying the gas with solution of potash. From half an ounce of ferrocyanide of potassium we obtained about 250 cubic inches of pure carbonic oxide. The probability is that the carbonic and sulphurous acids are the result of a subsidiary process. The carbon of the cyanogen is almost entirely oxidized into carbonic oxide at the expense of water, whilst the hydrogen of the water combines with the nitrogen of the cyanogen to form ammonia. But besides this, a portion of the carbon reduces the sulphuric acid to sulphurous acid, and thus becomes converted into carbonic acid, which accounts for the occurrence of these gases at the commencement.—Liebig's *Annalen*, April 1856, p. 127.

On the Solubility of Bones in Water. By Prof. Wöhler.

When bone-dust, such as is commonly employed as manure, is left for some time in contact with water, and the latter is filtered away, it is found to contain appreciable quantities of the phosphates of lime and magnesia. The same result is obtained when the water is freed from carbonic acid by long boiling. By filtering water for months through the same mass of bone-dust, it was found constantly to contain these earthy phosphates, and their quantity even appeared to increase in proportion as the organic matter of the bones became putrid in consequence of its long contact with water and air, and the water flowing off became turbid and offensive. This fact seems to have some practical value in agriculture, as it shows that without any artificial preparation the earthy phosphates may be extracted from the bones and introduced into the soil in a state of solution, perhaps exactly in the quantity necessary for their appointed functions, and that in the employment of bone-dust as manure, all the preparation necessary is perhaps to lay it in heaps during the summer and keep it constantly moist.—Liebig's *Annalen*, April 1856, p. 143.

On the Earthy Phosphates of the Urine. By Dr. C. Neubauer.

The author has investigated the urine for earthy phosphates, with a view particularly to answering the following questions:—

1. Do the quantities of phosphates of lime and magnesia daily evacuated in the urine stand in any determinate proportion to each other, or are their relative quantities subject to such variations that no determinate proportion can be derived from them?

2. What quantities of the phosphates of lime or magnesia are evacuated in twenty-four hours from different healthy men under the ordinary conditions of life?

3. Do lime-salts, taken internally, cause an increase of the normal quantity of the earthy phosphates? and, if so, how great is their influence?

In his introduction, the author states that he was induced to take up this investigation by Beneke's numerous observations upon the separation of the earthy phosphates, especially in pathological conditions*. He thinks that the reason why so little attention has been paid in the previous numerous analyses of urine to the earthy phosphates, is to be found particularly in the circumstance that the modes of determination still leave much to be desired both as regards accuracy and the time occupied in their execution. In his experiments the author followed neither the ordinary old method nor the one recommended by Vogel, but adopted the following process, which he considers to be free from considerable sources of error.

The urine is always collected for exactly twenty-four hours, and a portion of it is filtered. 200 cub. centims. are then mixed with ammonia until a strong precipitate is produced; this is caused to disappear by the careful addition of acetic acid, and the lime is precipitated from the fluid thus prepared by oxalate of ammonia. In the course of a few hours the oxalate of lime will be completely deposited and the supernatant fluid perfectly clear, so that it may be conveniently drawn off with a siphon, which, when it can be done without loss, is always to be preferred to the slow process of filtration. The oxalate of lime is afterwards collected upon a small filter free from lime, washed, dried, and calcined in a platinum crucible, until the carbon is entirely burnt away. The contents of the crucible are introduced carefully into a small flask, and receive an addition of 10 cub. centims. of a normal muriatic acid, of which each cubic centimetre represents 10 milligrms. of lime, or 18·49 milligrms. of $3CaO, PO^5$; the flask is warmed until the solution of its contents, and the excess of muriatic acid determined, after the addition of tincture of litmus, by a solution of soda of equivalent strength. The quantity of $3CaO, PO^5$ in 200 cub. centims. of urine may then be easily calculated from the number of cubic centimetres of acid saturated, and from this the amount of the salt contained in the urine of twenty-four hours.

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* Beneke, der Phosphorsaure Kalk in Physiolog. und Therapeut. Beziehun . Göttingen, 1850.

Another 200 cub. centims. of the filtered urine is precipitated with ammonia, and left for several hours for the complete separation of the whole of the earthy phosphates. The fluid is drawn off with a siphon, and the precipitate collected on a filter, the constitution of the ash of which has been determined; here it is washed with water to which one-fourth of ammonia has been added, dried, calcined, and weighed. The precipitate thus produced by ammonia always however contains organic substances, especially uric acid, which during calcination form a coal which is burnt away with difficulty. In the calcination of this precipitate therefore the following process is adopted. After the filter has been freed as completely as possible from the precipitate, it is folded together, a thin platinum wire is twisted spirally round it, and it is burnt in the upper or oxidizing cone of the flame. The operation is by this means considerably facilitated and abridged, and the ashes very soon become perfectly pure and white. A small fragment of nitrate of ammonia moistened with a drop of water is then laid upon the earthy phosphates in the crucible, dried, heated at first gently, but afterwards to the strongest red heat. The carbon disappears entirely, and the entire quantity of the earthy phosphates is thus obtained of a dazzling whiteness. If, from the quantity obtained by this second operation, the found quantity of phosphate of lime be deducted, the amount of pyrophosphate of magnesia in 200 cub. centims. of urine is obtained, and from this the quantity contained in the urine of twenty-four hours may be calculated.

By the method here described the author has instituted a great number of experiments upon normal urine, and upon the urine of persons who for the purpose of these experiments had taken lime-salts, especially phosphate, acetate, carbonate, and muriate of lime. The results are as follows:—

1. In the normal state, from men of twenty to twenty-five years, with a mixed diet, the quantity of earthy phosphates evacuated in twenty-four hours, on the average of fifty-two observations, was 0·9441 to 1·012 grm. The maximum was on the average 1·138 to 1·263 grm.; in one instance only was 1·554 grm. evacuated. The average minimum was 0·8 grm., and once only 0·328 grm. occurred.

2. The phosphate of lime, on an average of fifty-two determinations, amounted to 0·31 to 0·37 grm. The maximum was on the average 0·39 to 0·52, and only once 0·616 grm. The minimum was pretty constantly 0·25 grm., only once 0·15 grm.

3. The phosphate of magnesia, on the average of fifty-two experiments, was 0·64 grm. The average maximum was 0·77 grm., and once 0·938 grm. was passed. The average minimum was 0·5, but once sank to 0·178 grm.

4. In the normal state the average proportions of the two phos-

phates are 1 equiv. $3CaO, PO^5$ to 3 equivs. $2MgO, PO^5$. In 100 parts they consist on an average of 67 per cent. of phosphate of lime and 33 per cent. of phosphate of magnesia.

5. Lime-salts, when administered, do not pass into the urine, or only in very small quantity, the entire normal amount of secreted phosphates exhibiting no considerable increase during their administration.

6. In disease, the absolute quantity of earthy phosphates, as well as their relative proportions, appear to differ greatly from the normal evacuation.—*Journ. für Prakt. Chem.*, lxvii. p. 65.

On Soft Sulphur. By E. BAUDRIMONT.

When fresh soft sulphur is brought in contact with essence of turpentine in a closed tube, and left to itself for five or six days, the fragments of sulphur become opake, and covered with a great number of small, transparent, and brilliant crystals, which also clothe the walls of the tube. In a few months these crystals acquire a considerable size, which they do not afterwards appear to exceed. They are modifications of the symmetrical octohedron, which is always obtained when sulphur is crystallized at the ordinary temperature. As this crystallization takes place at the surface of the sulphur, and not in its mass, it cannot be attributed to a direct conversion of the soft sulphur into octohedric sulphur, but rather to the greater solubility of the former in turpentine and its return to the latter condition in this fluid, which would necessitate the precipitation of a portion of the body dissolved in the turpentine.

The author found that at 59° F. the same quantity of turpentine dissolved in twenty-four hours 100 parts of ordinary sulphur and 162 parts of soft sulphur. At 212° F. the soft sulphur appears to become converted into ordinary sulphur; and soft sulphur appears to possess different degrees of solubility, according as it was exposed to different temperatures and as it was more or less fresh.—*Comptes Rendus*, April 28, 1856, p. 808.

On some Compounds of Æthylamine. By Dr. EMIL MEYER.

Separation of Æthylamine from Ammonia.—The mixed solution of the two bodies is supersaturated with tartaric acid. The acid tartrate of æthylamine does not crystallize, but forms when evaporated a yellow syrup, which on cooling solidifies into an amorphous resinous mass; it is very readily soluble in alcohol, and can therefore be easily separated by it from the bitartrate of ammonia.

Separation of Oxide of Iron from Alumina by means of Æthylamine.—Æthylamine only throws down peroxide of iron, and not alumina, when it is added in excess to the solution of the two bases. The solution is filtered off, and the alumina obtained by calcination, or precipitated by carbonate of ammonia from the solution acidulated with muriatic acid.

Sulphate of Æthylamine and Sulphate of Magnesia and Æthylamine.—If a solution of sulphate of æthylamine, which is rather deliquescent and crystallizes with difficulty, be boiled, a distinct odour of æthylamine is perceived. When distilled in a retort, perceptible quantities of the base pass over, whilst the residue deposits a humus-like mass, and acquires an acid reaction. Formation of ammonia does not take place.

This salt combines with sulphate of magnesia to form a crystallizable double salt. If the solutions of the two salts be mixed in such proportions that the salt of æthylamine may be in excess, a syrup is obtained which is precipitated by alcohol. After standing for some time, crystals separate, which are freed by washing with alcohol from the excess of the salt of æthylamine, and may then be obtained pure by recrystallization. They form transparent columns. The author analysed this double salt, but the analyses leave it doubtful whether the salt contains 6 or 7 atoms of water of crystallization. They gave—

		Calculated with 7HO.		Calculated with 6HO.	
MgO	8·96	1	9·26	1	9·61
SO^3	36·52	2	30·84	2	34·86
C^4H^7N,HO	54·52	1	24·83	4	25·95
HO........		7	28·97	6	25·96

Double salts are also obtained with sulphate and chloride of copper.

Phosphate of Æthylamine and Magnesia.—When salts of æthylamine are present in solutions of salts of magnesia, the magnesia is not thrown down by the ordinary precipitants. Phosphate of soda however produces a voluminous precipitate in such a solution, but this after standing some time becomes crystalline. The salt is far more soluble than the corresponding ammonia-salt. This compound is of very little stability, for even over sulphuric acid it loses the whole of its water and a part of its æthylamine, whilst a further portion of the latter goes off at 212° F., as appears from the following experiments. The substance dried over sulphuric acid lost 18·22 per cent. at 212° F., and when calcined left 72·46 per cent. $(MgO)^2PO^5$. These crystals appear to have the composition $(MgO)^2,(C^4H^7N),PO^5+10HO$.

Sulphate of Alumina and Æthylamine.—The author has prepared this compound, and confirms Von Alth's previous statements regarding it. The crystals are fine octahedra, sometimes prisms which fall into octahedra on recrystallization.

Molybdate of Æthylamine.—Molybdic acid readily dissolves in æthylamine. When evaporated over chloride of calcium, white scales are separated, which when dried become reddish-brown, and also acquire a brown colour by lying. The molybdic acid contained in them was determined partly as Mo, and partly by calcination with a weighed quantity of oxide of lead, and oxidizing the residue by nitric acid. The æthylamine was determined by perchloride of platinum. The crystals constantly lose æthylamine with formation of a more acid salt. Analysis:—

MoO^3	72·22	73·03	2	72·23
C^4H^7N,HO	27·77	..	1	27·77

Phosphomolybdate of Æthylamine.—Phosphomolybdic acid, recommended by Sonnenschein as a test for ammonia, also produces a yellow precipitate in solutions of æthylamine. It is however of a paler colour, and of a caseous flocculent nature. It is more soluble in water, acids, and saline solutions than the corresponding ammoniacal precipitate, but is also amorphous. The other volatile bases, as well as many alkaloids, behave in a similar manner.

In its behaviour towards the salts of mercury, æthylamine differs remarkably from ammonia. If a solution of mercury be precipitated by æthylamine in such a way that the former may be in excess, a white precipitate is thrown down, which cannot be completely washed, as it constantly loses mercury. Its analysis gave—

Hg	75·03	per cent.
Cl	15·21	...

Æthylamine and oxygen are also contained in it. If an excess of æthylamine be employed in the preparation of the precipitate, another product is obtained. Thus if perchloride of mercury be dropped into æthylamine, a yellowish precipitate is formed; this becomes white when more chloride is dropped in, and again becomes yellow by stirring. This precipitate is flocculent, and insoluble in water, so that it may easily be washed. It is difficult of solution in acids, although its external appearance is modified by every acid. It dissolves most readily in muriatic acid. No æthylamine is evolved from it by potash, but its colour becomes brownish-yellow. Its analysis gave—

Hg	85·65
Cl	8·52
C	1·38
H	0·34
N	0·80
O	3·31

No formula can be derived with certainty from these numbers.

Biæthylamine and triæthylamine furnished with perchloride of mercury similar precipitates of corresponding per-centage composition, from which however it was equally impossible to deduce a rational formula, as they probably consist of a mixture of various compounds.

The non-volatile oxide of tetræthylammonium behaves very differently towards perchloride of mercury, pure oxide, or when the alkali contains carbonic acid, a mixture of oxide and chloride being thrown down. In one case it was $HgCl + 3Hg$.—*Journ. für Prakt. Chem.*, lxvii. p. 147.

Facts towards the History of Ætherification.
By ALVARO REYNOSO.

Action of Binoxide of Mercury upon Hydriodic-æthylic Æther.

1. When binoxide of mercury and hydriodic æther are sealed up in a glass tube, and heated for four hours to 500° F., a very ener-

getic reaction takes place. Through the sides of the tube the mass is seen to be decomposed and blackened, containing a few globules of metallic mercury at the bottom of a very mobile fluid. On opening the tube a great evolution of gas takes place, followed by a strong explosion, which rendered it impossible to ascertain the nature of the reaction, except that a portion of the iodine had been set free.

2. Binoxide of mercury was sealed up in a tube with hydriodic æther, and kept at 212° F. for six hours; the binoxide had become converted into iodide, and when the tube was opened it was found that there was,—1st, formation of olefiant gas; 2ndly, production of hydric æther; 3rdly, formation of a trace of acetic acid; 4thly, a residue of undecomposed hydriodic æther; 5thly, a little iodide of mercury in solution in the æther.

3. A tube containing hydriodic æther and binoxide of mercury was left for seventeen months at a window, through which the rays of the sun entered with facility. In a few days the reaction had commenced, to judge by the formation of iodide of mercury, which increased daily, becoming deposited in fine crystals upon the walls of the tube. When the tube was opened, a considerable quantity of gas was evolved; the liquid product was composed principally of acetic æther, with a small quantity of hydric æther. The formation of acetic æther is evidently due to a secondary reaction, the binoxide of mercury first converting the hydriodic æther into ordinary æther. The acetic æther would be produced by an oxidation of the hydric æther, which could only take place at the expense of the oxygen of the oxide. This causes the formation of metallic mercury, or of a lower oxide of this metal. It is probable that metallic mercury is set free, which then acts in its turn upon the undecomposed hydriodic æther, forming, as indicated by Frankland, iodide of mercury, together with a gaseous mixture of æthyle, hydruret of æthyle, and olefiant gas.

If to the above result we add the production of hydric æther by the action of water (Frankland) and oxide of silver (Wurtz), we may hope to obtain the same action with other oxides. This may have no very great interest as regards the production of æther, but this is not the case when we consider the important part it may play in the explanation of the ætherification of alcohol by many bodies, the action of which is not yet well known. It is probable that other oxides will react in the same way upon hydrochloric and hydrobromic æthers.

Action of Sulphates upon Alcohol.—The sulphates of magnesia, manganese, iron, cobalt, nickel, cadmium, zinc, and copper were placed with alcohol in sealed tubes, the latter enclosed in a gun-barrel, and heated to 464° F. in an oil-bath. They all produced the ætherification of the alcohol, but none, with the exception of those of nickel and copper, underwent any decomposition. The sulphate of nickel was converted into subsulphate, and that of copper was partially reduced to the metallic state. There was no evolution of gas except with sulphate of copper, when a large quantity of gas is set free on the tube being opened. The undecomposed sulphates retain all their chemical properties, and dissolve completely in water. Crystallized sulphates were always employed. They all lose their water of crystallization by the combined action of the heat and alcohol, and in this anhydrous state they dissolve more slowly in water.

Iodides and Bromides.—Iodide and bromide of cadmium, heated to 464° F. with alcohol, produce æther. They are not decomposed, and when the tube is opened no gas is disengaged. Bromide of mercury was heated with alcohol to 464° F. The mass became strongly blackened; when the tube was opened there was a great evolution of gas, and the alcohol was ætherified. The bromide was decomposed.

Chlorides and Muriates.—The chlorides of cobalt and cadmium and the protochloride of manganese, heated to 464° F. with alcohol, remain without decomposition, and the alcohol is converted into æther without disengagement of gas. Protochloride of manganese produces the greatest quantity of æther.

Chloride of nickel, under the same circumstances, becomes converted into insoluble subchloride; the alcohol produces æther, and on opening the tube there is a slight evolution of gas.

Protochloride of tin was heated to 464° F. with alcohol, and after the experiment the liquid in the tube was separated into two very distinct strata,—the upper one limpid, the inferior milky. Gases were evolved on opening the tube, and a large quantity of æther was formed.

Protochloride of iron, used in the same way, produces a very marked action. The liquid in the tube separates into two very distinct strata, of which the upper and largest one consists of pure æther. On opening the tube there is a slight evolution of gas. Protochloride of copper also causes the ætherification of alcohol.

Bichloride of mercury, heated with alcohol to 464° or 392° F., is decomposed; the mass becomes greatly blackened, and when the tube is opened a great quantity of gas is evolved. Æther is formed.

The muriates of morphine and cinchonine, heated to 392° F. with alcohol, become black; there is no disengagement of gas on the tube being opened, and the liquid contains but a small proportion of æther. The ætherial odour is more strongly marked with cinchonine than with morphine.—*Comptes Rendus*, April 14, 1856, p. 686.

On the Preparation of Cumarine. By Dr. GÖSSMANN.

Cumarine may be advantageously obtained in the following simple manner:—Finely cut Tonquin beans are heated for a long time nearly to boiling with about an equal volume of alcohol of spec. grav. 863; the fluid is then filtered off, and the residue repeatedly treated in the same way. The solutions are mixed, and the alcohol distilled off until the residue begins to grow turbid, when about four times its volume of water is added, by which the cumarine is thrown down in a crystalline form. The mixture is then heated to boiling, and the solution passed through a filter moistened with water. On this the fatty matter which is thrown down at the same time remains, whilst pure cumarine crystallizes from the solution on its cooling. The remainder is obtained by the concentration of the mother-liquor; and if it be not quite colourless, it may be procured perfectly pure by treatment with animal charcoal. In this way more than 7 grms. of cumarine have been obtained from 1 lb. of Tonquin beans.—Liebig's *Annalen*, April 1856, p. 66.

On the Preparation of pure Silver from Silver containing Copper. *By* Dr. W. Wicke.

The alloy is dissolved in nitric acid, the excess of acid evaporated, the solution diluted with water, and the two oxides precipitated by an excess of carbonate of soda with the assistance of heat. The two carbonates are then reduced with the aid of heat by a solution of grape-sugar, the copper in the form of protoxide, the silver in the metallic state. The reduction commenced immediately; but to make sure of the reduction of all the carbonate of silver, the boiling must be continued for some time. The precipitate is filtered, and whilst still moist treated with hot carbonate of ammonia. The copper is dissolved, but the silver remains in a pure state. The treatment with carbonate of ammonia is continued as long as the solution acquires a blue colour. Washing is effected by decantation.

If the silver be not entirely reduced, silver is also dissolved by the carbonate of ammonia. In my experiments no silver existed in the filtrate. The boiling with grape-sugar was continued about ten minutes.

Instead of carbonate of soda, the two metals may also be precipitated by potash, and the reduction effected with the oxides. The process is simple, and takes but little time.—Liebig's *Annalen*, April 1856, p. 143.

ANALYTICAL CHEMISTRY.

On a Mode of determining Copper. *By* Dr. T. Fleitmann.

In November 1855 Dr. Mohr described a simple method of determining copper*, on reading which I regretted that I had not made known a method which I have made use of with great advantage for several years, and which appears to me to be preferable to that just mentioned, as well as to the process of reducing protoxide of copper by means of grape-sugar, and subsequent volumetric determination, especially, in many cases, when it is desired to arrive quickly at the result.

When the solution of copper is free from nitric acid, or injurious metals, such as antimony and arsenic, I precipitate it with pure metallic zinc, get rid of the excess of zinc by digestion with pure dilute sulphuric acid, wash the precipitate of copper, if iron were present, with boiled water, and dissolve it in an acid solution of pure perchloride of iron. The solution of the copper takes place almost instantaneously, and furnishes double its equivalent of protoxide of iron, which is determined in the well-known way by permanganate of potash.

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* Chem. Gaz., vol. xiii. p. 73.

To solutions in which the precipitation of the copper is rendered difficult by the presence of nitric acid, I add an excess of ammonia, filter from any peroxide of iron (or oxide of bismuth or lead) that may be present, and effect the precipitation of the copper in the ammoniacal solution by means of fine zinc filings or shavings. It takes place pretty rapidly with the aid of a little heat, and its completion is to be recognized in solutions free from nickel, by the entire disappearance of the blue colour. The copper thus precipitated is first freed from nitrates by washing, and afterwards from the excess of zinc by digestion with dilute sulphuric acid. The rest of the process is the same as above described. To get rid of the nitric acid by means of zinc, as recommended by Mohr, requires a large quantity of zinc when much nitric acid is present; and the smallest trace of lead, antimony, or arsenic in the zinc renders the result of the determination inexact.

Precipitation in an ammoniacal solution also enables copper to be determined in the presence of arsenic, which so often accompanies it. In this case the arsenic is converted into arsenic acid, an excess of ammonia is added, the arsenic acid is precipitated by sulphate of magnesia, and the filtered cupreous solution is treated as above described.—Liebig's *Annalen*, April 1856, p. 141.

On the Detection of Iodine in Mineral Springs. By J. Liebig.

When a very small quantity of an alkaline iodate, followed by sulphuric or muriatic acid, is added to a fluid which contains so small a quantity of metallic iodides that no distinct blue coloration can be obtained by starch and nitric acid, a far stronger reaction is obtained; hydriodic acid and iodic acid being separated, which become mutually converted into water and iodine, so that the amount of iodine set free is increased by the iodic acid added. Neither iodic acid nor iodide of potassium mixed with muriatic acid, colours starch.

When the mother-liquor of a mineral spring was mixed with starch-paste and muriatic acid, with the intention of adding iodic acid to it afterwards, the author observed that it produced as fine a blue colour as can be produced by any of the known methods, by means of chlorine-water, hyponitrous acid, &c. The water of the Adelheid spring, the mother-liquor of the Reichenhall bath, and in fact all the waters containing iodine which he examined, behaved in exactly the same manner; with starch-paste, and the addition of pure muriatic acid free from chlorine and iron, they gave as distinct a reaction as can be obtained with other very delicate reagents.

The same muriatic acid gives not the least colour with iodide of potassium and starch-paste, so that some body must exist in these waters which sets free the iodine of the iodide, or the liberated hydriodic acid, on the addition of a mineral acid. It seems probable that this may be due to the presence of nitrates, which the author found in these waters, and frequently in large proportion; but he does not feel certain that these are the cause of the reaction, as by mixing such salts with iodide of potassium, and adding starch-paste and muriatic acid, the reactions were not nearly so delicate as with the mother-liquors, although the latter contained much more iodine in the form of iodides, than was employed in his experiments. The mother-liquors were free from persalts of iron, which might have caused the reaction.—Liebig's *Annalen*, April 1856, p. 51.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Silvering and Gilding of Glass. *By* J. Liebig.

Silvering Glass.—At the request of M. von Steinheil, the author has made some experiments to discover a process for silvering glass *in the cold*, especially with a view to the production of faultless optical mirrors. The silvering fluid, which perfectly fulfils the desired end, is an ammoniacal solution of nitrate of silver with an addition of caustic potash or soda, which, when mixed with a solution of sugar of milk in water at ordinary temperatures, deposits the silver on the surface of the glass in the form of a mirror.

To prepare the fluid, 10 grms. of fused nitrate of silver are dissolved in 200 cub. centims. of water, and a sufficient amount of liquid ammonia is added to produce a clear solution. This is gradually diluted with 450 cub. centims. of a solution of potash of spec. grav. 1·05, or with the same volume of a solution of soda of 1·035. On the addition of this, a blackish-brown precipitate is usually produced, which must be at once dissolved by a fresh addition of liquid ammonia. The mixture is diluted with so much water as to bring it to 1450 cub. centims. A dilute solution of nitrate of silver is then dropped in until the production of a strong gray precipitate (not turbidity), when the mixture is brought to 1500 cub. centims. by the addition of water. Each cubic centimetre thus contains a little more than 6·66 milligrms. of nitrate of silver, or 4·18 milligrms. of silver. To produce a clean mirror, the fluid should contain no free ammonia, but this must be completely saturated with oxide of silver. For this purpose some of the solution of silver may be kept back and added at the end; and in this case 1 cub. centim. of the solution contains rather less than 4·18 milligrms. of silver.

The solution of potash or soda must be free from chlorides; pure carbonate of soda or potash must be dissolved in water, and rendered caustic by hydrate of lime previously freed from all chloride by washing with distilled water. The solution is not filtered, but left to stand until it becomes perfectly clear.

Immediately before the application of this fluid, it is mixed with one-tenth to one-eighth of its volume of solution of sugar of milk, containing 1 part in 10 parts of water.

In silvering small concave or convex mirrors, a stick or brass hook is attached to the back of the glass by a resinous cement, so as to enable the glass to be suspended horizontally. It is suspended over a suitable glass or porcelain saucer, with the surface to be silvered about half an inch from the bottom of the vessel, and the fluid previously mixed with the solution of sugar of milk is poured in until the whole surface of the glass is immersed.

For the production of flat mirrors the author recommends vessels of gutta percha, cut out of a flat piece so as to have a margin of about an inch all round the glass. This is turned up after the gutta-percha has been softened in hot water, and the corners are made water-tight by the application of a hot spatula or knife. The glass is supported, at a distance of half an inch from the bottom of the vessel, by means of small cones of gutta percha at the corners, and the space between the surface of the glass and the bottom is then filled with the silvering fluid. The author admits that these arrangements are very imperfect, and that many improvements might be introduced, but the glass should always be suspended at the surface of the fluid.

The reduction of the silver takes place instantly upon the mixture of the alkaline solution of silver with the sugar of milk; the mixture immediately acquires a dark colour. In a few minutes the glass plate appears black; in a quarter of an hour it becomes bright, and the reduction is complete when the fluid between the edge of the glass and the wall of the vessel is covered with a white specular coat of silver. Of course the whole of the silver in the solution is precipitated, and only a very small portion of it goes to form the mirror. The quantity of silver attached to a surface of 226 square centims. was 49 milligrms. The silvering of a mirror of 1 metre square would consequently take 2·210 grms. of silver. The quantity of fluid required to silver a glass of 226 square centims. was 280 cub. centims., containing 1170 milligrms. of silver, so that 1170—49 =1121 milligrms. of silver are thrown down in the fluid and on the walls of the vessel; this must be collected, and again converted into nitrate of silver, and some loss is unavoidable.

When silvered, the glass plate is taken out of the fluid, washed with warm distilled water, and dried in a warm place. Care must be taken, in removing and washing the plate, not to injure the silver coat with the fingers, as otherwise the water penetrates by capillary attraction through the injured spot, and separates the coat of silver from the glass. When dried, the silver adheres so strongly to the glass that it can hardly be rubbed off with the finger. It forms a very beautiful, somewhat opalescent mirror, which may be converted into a perfect silver mirror by careful polishing with fine rouge and velvet. A good deal depends on the cleaning of the glass in the production of perfect mirrors.

The distance between the bottom of the vessel and the surface of the glass must be exactly equal throughout, as otherwise the thickness of the coat of silver will be unequal, and the places where it is thinnest will appear darker than the rest. The smallest bubble of air also will cause a small vacancy in the coating, and the author has found it advantageous to moisten the surface of the glass in the first place with alcohol, as this displaces the adherent stratum of air more readily than water.

When placed at the bottom of the vessel the glass plate is just as completely coated, but the whole of the silver in the solution is precipitated upon it in the form of a gray powder, which adheres so strongly that it can only be got rid of by mechanical means, which endanger the mirror itself. The cost is also greatly increased.

Before putting it into a frame, the dry mirror is warmed a little, and coated with a thin colourless varnish. For this purpose a solution of dammara resin in alcohol is very good.

Gilding of Glass.—Glass can only be permanently and brilliantly gilt with the assistance of heat. Gilding effected in the cold is of beautiful colour and lustre, but does not adhere, and detaches itself from the glass by washing with water.

The gilding fluid is prepared by dissolving pure gold in nitromuriatic acid, adding 292 milligrms. of chloride of sodium to the solution for every gramme of gold, evaporating to dryness, and heating the residue until all free acid is driven off. The double salt is then dissolved in water, and water is added until each 100 cub. centims. of fluid contains exactly 1 grm. of gold. 50 cub. centims. of this solution are mixed with 20 cub. centims. of a solution of soda of spec. grav. 1·035, and 300 cub. centims. of water in a glass flask, and boiled until it is reduced to 250 cub. centims.; and another 50 cub. centims. of the solution, mixed with 20 cub. centims. of the same solution of soda and 230 cub. centims. of water, are kept for an hour in boiling water. The two fluids are then mixed together, and must be employed in gilding whilst fresh.

To gild the inside of a glass vessel, a tenth part of its volume of a mixture of 2 parts of alcohol and 1 part of æther is poured into it, and it is then filled up with the hot gold solution. The vessel is then set in water, the temperature of which must not rise above 176° F. In from ten to fifteen minutes its inner surface is covered with a brilliant golden film, and the vessel is removed from the water when its walls are opake, or exhibit a deep green colour by transmitted light.

The alkaline solution of gold is of course always reduced by the alcohol, but the glass only acquires its brilliant golden coat when the fluid is of such a nature that the adhesion of the gold to the glass may be somewhat stronger than that to the water; in the former case the gold is precipitated only on the glass, in the latter only in the fluid. It is very difficult to hit this point exactly, and the smallest error in the mixture renders success impossible. The author adds, that he has obtained the most beautiful gilding by this means, whilst in other cases he has failed entirely, without being able to discover the cause, so that he does not think this method will be of general application. The mixture will only act whilst fresh, when it has a very slight yellowish tinge; by standing it becomes colourless. Alcohol reduces the gold from the colourless fluid with difficulty.—Liebig's *Annalen*, April 1856, p. 132.

Analyses of Bronze. By C. H. BURBIDGE HAMBLY, F.G.S.*

The following examination was made in the Metallurgical Laboratory of the School of Mines, Museum of Practical Geology, to ascertain whether specimens taken from different parts of a large bronze casting would show by analysis identity of composition.

The casting from which the specimens were obtained was a colossal statue; one portion was taken from the "sow, or feeding runner," which is the highest part of the casting, and the last to cool; a second portion was taken from the "bottom runner," which is the lowest portion of the casting, and the first to cool; and a third portion was taken from the middle of the front of the statue.

The piece from the "sow runner," when fractured, presented an extremely irregular surface, varying in colour, due to the separation of a white alloy; the better to secure a fair sample for analysis, small fragments were broken off from different parts of the specimen.

The piece from the "bottom runner," when fractured, showed a compact uniform surface.

The piece taken from the statue was also compact and uniform in structure.

In addition to these three specimens, an analysis was made of a piece of the white alloy, which is mixed and melted previously to the formation of the bronze metal.

The analyses were conducted in the following manner:—A weighed portion of the alloy was digested in nitric acid, the solution evaporated to dryness, and the insoluble residue weighed as oxide of tin; the filtrate, after the addition of sulphuric acid, was evaporated to dryness, and the precipitate weighed as sulphate of lead. Sulphuretted hydrogen was passed through the filtrate, the precipitate collected on a filter, redissolved, precipitated by caustic potash, and weighed as oxide of copper; ammonia was added to the sulphuretted hydrogen filtrate, and the precipitate weighed as peroxide of iron; the filtrate was evaporated to dryness to expel ammonia-salts, the residue redissolved in acid, carbonate of soda added, and the precipitate weighed as oxide of zinc.

To estimate the sulphur, a fresh portion of the alloy was digested in nitrohydrochloric acid (care being taken to prevent any large excess of nitric acid being present), the globule of sulphur collected and weighed, chloride of barium added to the solution, and the remainder of the sulphur estimated from the weighed precipitate of sulphate of baryta.

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* Communicated by the Author.

A portion of the alloy was tested for antimony by means of the hydrogen apparatus, and the presence of a trace discovered.

Results of the Analyses.

	Top runner.	Bottom runner.	Statue.	White alloy.
Copper	83·37	82·28	83·33	42·78
Tin with trace of antimony	4·48	4·75	4·28	29·48
Lead	3·99	4·32	3·96	1·60
Zinc	6·42	7·07	6·26	26·48
Iron	0·45	0·48	0·42	trace
Sulphur	0·30	0·28	0·30	0·41
	99·01	99·18	98·55	100·75

Theoretical and Practical Investigation on the Fixation of Colours in Dyeing. By FREDERICK KUHLMANN. (Part II.)

The author having found, as stated in the first part of this paper*, that pyroxyline, when deprived of a portion of its nitrous elements by spontaneous decomposition, acquired a capability of taking dyes quite opposite to that possessed by pyroxyline, commenced a fresh series of experiments with cotton stuffs, which before receiving the mordant had been in contact for a longer or shorter time either with nitric acid of various degrees of concentration, or with variable mixtures of nitric and sulphuric acids. The results were very remarkable. With Brazil wood, acetate of alumina gave violet-red tints upon non-azotized cotton; immersion for twenty minutes in nitric acid of 34°, followed by washing with a large quantity of water, and immersion in a weak solution of carbonate of soda before the application of the mordant, gave a far deeper and less violet-red colour than that taken by the cotton which was not prepared with acid. The result was confirmed by several successive trials. A very sensible effect was produced, even by the immersion of the cotton for half an hour, in the same acid diluted with double its volume of water; and in this case the tenacity of the cotton was not perceptibly altered.

In the following comparative experiments—

No. 1 was cotton without any acid preparation;

No. 2, cotton kept for five minutes in a mixture of 2 vols. of nitric acid of 34° and 1 vol. of sulphuric acid of 66°;

No. 3, cotton kept for two minutes in a mixture of 1 vol. of nitric acid and 1 vol. of sulphuric acid;

No. 4, cotton kept for twenty minutes in a mixture of 1 vol. of nitric acid and 2 vols. of sulphuric acid;

No. 5, cotton kept for twenty minutes in a mixture of 1 vol. of nitric acid, 2 vols. of sulphuric acid, and ½ vol. of water.

After the acid baths, the stuffs were washed with a large quantity of water, passed into a bath of carbonate of soda, washed again, and finally passed into a mordant of acetate of alumina. The dyeing was effected with a decoction of Brazil wood.

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* Page 192.

No. 1 took a pale violet-red colour;
No. 2, a less violet-red tint, but still rather pale;
No. 3, a deeper and brighter colour;
No. 4, a much deeper poppy-red colour, very like that obtained with the decomposed pyroxyline;
No. 5, a deep red colour of extraordinary richness. Under the same circumstances, but with a stronger dye-bath, a splendid red colour was produced of such depth that it appeared brown. The same results were obtained in several repetitions of the experiments.

From this it evidently follows that a mixture of sulphuric and nitric acids furnishes colours most approaching scarlet, and that the best results are obtained with a bath consisting of 1 vol. of nitric acid of 34°, 2 vols. of sulphuric acid of 66°, and ½ vol. of water.

The author also made some comparative trials of dyeing with cochineal and orchil upon cotton. The mordant was acetate of alumina. Immersion of the cotton for twenty minutes in a bath of pure nitric acid, or a mixture of 2 vols. of nitric acid and 1 vol. of sulphuric acid, gave with cochineal a pale red tint, very like that produced without an acid bath. The same immersion in a bath of 1 vol. of nitric and 1 vol. of sulphuric acid gave a much deeper colour. A mixture of 1 vol. of nitric and 2 vols. of sulphuric acid gave a colour of at least double the intensity of the preceding.

With the last acid mixture also a pretty strong colour was obtained upon cotton with orchil.

With garancine a bath of nitric acid alone gave a yellower but not a deeper tint than upon cotton which had not been azotized. 2 vols. of nitric and 1 vol. of sulphuric acid gave a similar tint, but deeper than the preceding. Equal volumes of the acids gave a very fine brownish-red colour, like the Adrianople-red before avirage. 1 vol. of nitric and 2 vols. of sulphuric acid gave the same intensity of colour, but a shade more approaching orange. Lastly, twenty minutes' contact of the cotton with a mixture of 1 vol. of nitric acid, 2 vols. of sulphuric acid, and ½ vol. of water, gave a very bright red colour, of much greater intensity than the preceding.

All these experiments were repeated with wool, silk, feathers, and hair, previously submitted to the same treatment as the cotton, with remarkable results as regards the intensity and richness of the colours. Even with nitric acid diluted with 5 times its volume of water the effects are very distinct.

As in treatment with concentrated acids the threads or tissues, especially those of cotton or linen, are considerably altered, so that the preceding results cannot be generally applied in dyeing, the author attempted the fixation upon these tissues of different azotized matters produced by the action of concentrated nitric acid upon certain organic bodies. Picric acid, which does not attach itself to cotton with a mordant of alumina, gives very strong tints when the cotton has been nitrated. In this case the acid acts as a colouring matter, but it acts also as a mordant, especially in producing compound colours, either by using baths of picric acid after the application of the ordinary mordants, or by mixing the acid in variable quantities with the colour in the dye-bath. The colours thus produced are very bright, but they are more applicable to dyeing upon wool and silk, as upon cotton the picric acid reacts in time upon the colouring matter, usually causing it to become yellow.

The author considers that from these experiments it follows, that the chemical composition of the bodies to be dyed has the greatest influence upon the fixation of colour, that dyeing is a true chemical combination, and that the effects due to capillarity, and the peculiar structure of the material are but secondary. These theoretical points will be treated in the third part of his memoir.—*Comptes Rendus*, April 21, 1856, p. 711.

On the Preparation of Hydrate of Potash from Nitrate of Potash.
By Dr. A. GEUTHER.

Graf[*] and Riegel[†] have stated that the process recommended by Wöhler[‡] for the above purpose is useless, as the product always retains nitrate and nitrite of potash. The author observes that it would have been well if these gentlemen had repeated their experiments with a little more care, before publishing anything about them, as he can say, from his own experience, that the process readily furnishes pure hydrate of potash, perfectly free from nitrate and nitrite of potash.—Liebig's *Annalen*, xcvii. p. 223.

PATENT.

Patent granted to Robert Besley, *for an improved manufacture of Metallic Alloy, applicable to the casting of Type.*

THE object of this invention is to produce an alloy of a harder and tougher quality than that commonly used in the casting of metal types, and having the property (when in a molten state) of retaining its fluidity a sufficient time to ensure a good casting when run into moulds or dies, and of setting quickly when it has entered the moulds or dies.

It is well known that the alloy commonly used in the manufacture of printing types is composed of lead, tin, and antimony, combined in various proportions according to the judgement and requirements of the type-founder. The best metal that can be made by the admixture of these bodies is however an imperfect compound, wanting strength and continually deteriorating, while in a molten state, by the evaporation of that most important element, antimony, which action is taking place during the whole time that the manufacture is proceeding. Now in order to prevent this change in the quality of the same pot of metal, and to ensure the production of a series of castings that shall be perfectly homogeneous, the patentee proposes to add to the compound known as type-metal certain substances which possess the property of fixing the antimony and giving the alloy the other qualities which it seems to require. The substances employed for this purpose are nickel, which will impart hardness to the alloy, and copper, which, besides giving additional toughness, appears to act as a flux to the antimony, and ensures its complete amalgamation with the other metals. These metals, it is stated, may be in part displaced by others, which play a somewhat similar part in the formation of the improved alloy. Thus, by a diminution of the quantity of nickel, and the substitution, in lieu of the subtracted portion of nickel, of an equivalent portion of metallic cobalt, the required hardness will be obtained; and, further, by the addition of bismuth in place of a small quantity of copper (which, like the copper, also acts as a flux), a homogeneous compound is produced, and the quick setting of the alloy is ensured. It will thus be understood that the substances introduced, by preference, into the compound of lead, antimony, and tin, in order to obtain the objects above enumerated, are nickel, copper, metallic cobalt, and bismuth; the nickel and cobalt being the materials used to give hardness, and the copper being the medium by which these substances are caused to unite with the antimony of the common type-metal; while, by the introduction of the bismuth (which has the well-known property of passing instantly from fusing to fixity), the setting of the alloy is somewhat expedited.

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[*] Wittstein's Vierteljahresschrift, iv. 65.

[†] Neues Jahrbuch der Pharmacie, iii. 261.

[‡] Liebig's Annalen, lxxxvii. p. 373.

The proportions found best for the purpose contemplated are as follow:—

100	parts of good virgin lead.
30	... regulus of antimony.
20	... tin.
8	... nickel.
5	... metallic cobalt.
8	... copper.
2	... bismuth.

As nickel and cobalt will readily unite with copper, but will not form a perfect union with antimony, the nickel and cobalt are first melted with the copper and a small quantity of bismuth, and the mixture is then added to the alloy containing the antimony (with continued stirring), and the result will be a perfectly homogeneous compound.—Dated June 28th, 1855.

THE CHEMICAL GAZETTE.

No. CCCXXVIII.—June 16, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Potash-lime upon Palmitic Acid, and on the Nature of Crude Æthal. *By* Prof. W. Heintz.

In the last November Number of Liebig's 'Annalen[*],' Scharling has expressed the opinion, that the four acids (stearic, palmitic, myristic, and lauric acids), which I detected in the products of the action of potash-lime upon crude æthal at a temperature of 427° F., might very well have been produced in this operation from a single body, æthal ($C^{32}H^{34}O^2$). He states that he has also found butyric acid among the products of decomposition, which certainly could not have been produced from the corresponding alcohol, as otherwise the æthal must have possessed the odour of the latter. For further corroboration of the occurrence in this case of another plan of decomposition than that expressible by the formula $C^nH^{n+2}O^2+(KO+HO)=(C^nH^{n-1}O^3+KO)+4H$, Scharling allowed potash-lime to act upon palmitic acid at a temperature of 418° F., and found that the mass also contained butyric acid.

In the experiments which I have repeatedly made for the decomposition of crude æthal, in which the potash-lime compound obtained was always decomposed by boiling with dilute acid, I had never observed the odour of butyric acid, although it is so easily recognizable; but, on the other hand, I could not doubt that Scharling had actually found butyric acid in his experiments. I thought that this contradiction might be explained by supposing that Scharling had not sufficiently prevented the access of air to the heated mixture. In my experiments I had always excluded the air with the greatest care, as I supposed that at a temperature of 427° F. the oxygen might have an oxidizing action even upon a fatty acid in combination with a base. I have also expressly stated this in my paper upon æthal[†].

To ascertain whether my supposition was correct, I mixed 15 grms. of palmitic acid, fused over a few drops of hot water, with twice its amount of a mixture of the hydrates of potash and lime, divided the mixture, after it had been cooled and pulverized, into two equal parts, and poured these into two glass flasks, of which one had been previously filled with hydrogen gas. To this a gas tube filled with hydrogen gas was immediately attached by a cork, its other end communicating with a hydrogen gas apparatus, when by slightly loosening the cork the stream of gas was driven into the flask, and the air thus expelled. The cork was then carefully fastened, and the flask transferred to the metal-bath, which was heated to 427° F., whilst care was taken not to open the mouth of the gas-tube until it was immersed in mercury. The second flask was placed in the same metal-bath without being corked.

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[*] Vol. xcvi. p. 236.

[†] Chem. Gaz., vol. xiii. p. 31.

After the heat had been applied for five hours, the flasks were removed, but no gas had escaped from the flask which was furnished with a gas tube. The contents of the open flask had become considerably black near the surface, the lower part of the mass being quite colourless. From this it follows that the oxygen of the air had exerted a decomposing action. The contents of the other flask, which had been protected from the air, were perfectly white throughout. When this mass was decomposed by dilute sulphuric acid, I observed no trace of the odour of butyric acid. Even when I distilled the acid fluid from which the fatty acid had separated in a perfectly colourless state, together with the latter, supersaturated the distillate, which indeed was but slightly acid, with two drops of solution of carbonate of soda, evaporated it, and mixed the very small residue with a little dilute sulphuric acid, the odour of muriatic acid, evidently arising from the impurity of the hydrate of potash, could be distinctly perceived, but not that of butyric acid. On the addition of alcohol the odour of butyric æther was not evolved, even on the application of heat.

On the other hand, the mass taken out of the second flask diffused a strong odour of butyric acid as soon as it was decomposed with dilute sulphuric acid. On distillation an acid water passed over, which, when saturated with carbonate of soda (for which purpose far more than two drops of the solution was required) and evaporated, evolved a very strong odour of butyric acid on the addition of a little dilute sulphuric acid. The quantity of butyric acid however was too small to allow of its isolation. Nevertheless, on the addition of a little alcohol, the odour of the mixture changed immediately to that of butyric æther, which is so readily formed when butyric acid is agitated with alcohol, and even a little dilute sulphuric acid. I therefore have no doubt that the acid formed was really butyric acid.

I then investigated the fatty acids again separated from the potash-lime compound. That obtained from the contents of the flask filled with hydrogen gas was perfectly colourless, and possessed all the properties of the palmitic acid employed in the experiments, *and especially the same melting-point.* This acid therefore is not decomposed by potash-lime at a heat of 418° to 436° F. without access of air. The other acid obtained from the potash-lime mass, which had become brownish-black, and freed from volatile acid by distillation with water, was of a dark brownish-black colour and opake even in the fluid state. Its exact melting-point could not therefore be directly ascertained. I endeavoured to free it from the brown substance by solution in alcohol and filtration; but the acid separated again from the solution by means of water still retained its brown colour. I therefore treated its alcoholic solution with freshly calcined animal charcoal, filtered it, and precipitated the acid by water. It was then perfectly colourless, and its melting-point could be easily determined. It was *exactly the same* as that of the palmitic acid employed in the experiment. From this it follows that the oxidation which this acid undergoes when heated for a long time to 427° F. with potash-lime under the influence of the air, does not give rise to the formation of fatty acids incapable of volatilization with aqueous vapour, for otherwise the melting-point of the palmitic acid must have been lowered by this operation.

In a previous paper* I have shown that no evolution of gas takes place during the action of potash-lime upon non-volatile fatty acids even at 436° F. Hydrogen gas must however be evolved if butyric acid is produced from palmitic acid, unless the access of air be permitted,—partly hydrogen from the palmitic acid itself, and partly hydrogen from the hydrate-water of the hydrate of potash, the oxygen of which must serve for the oxidation of the carbon of the palmitic acid. The present experiments also show that no gas is evolved during this process. This circumstance is sufficient evidence against the supposition that palmitic acid can give origin to fatty acids with a less amount of carbon under the influence of potash-lime at 427° F. without access of air.

I have thus proved that under these circumstances a decomposition of palmitic acid only takes place by the action of the atmospheric oxygen. I therefore consider the supposition with which I started, that Scharling in his experiments did not sufficiently exclude the air, as fully proved. As I have always done this, and therefore never observed the formation of butyric acid in the operation, the foundation of Scharling's doubt of my assertion that crude æthal contains four alcohols is overthrown. But if volatile acids were really formed by the access of air to the potash-lime compound, the experiment has yet shown that palmitic acid exposed to the action of these substances, when freed from the volatile acids by distillation with water, again possessed exactly the same properties, and especially the same melting-point, as before, so that this decomposition gives rise only to volatile acids, but neither lauric, myristic, nor stearic acid can be produced. My conclusion is therefore completely confirmed, namely, that as amongst the products of the decomposition of crude æthal by potash-lime at 427° F. in the absence of air, I found not only palmitic acid, but also stearic, myristic, and lauric acids, crude æthal must contain four alcohols; namely, æthal ($C^{32}H^{34}O^2$), stethal ($C^{36}H^{38}O^2$), methal ($C^{28}H^{30}O^2$), and lethal ($C^{24}H^{26}O^2$).

Even if I were to admit the possibility that myristic and lauric acids may be formed by oxidation from palmitic acid, and that therefore experiments were necessary to prove that this was not the case in my experiments, I still cannot at all see how Scharling could have put forward the opinion, that stearic acid may also be formed from palmitic acid or æthal ($C^{32} H^{34} O^2$) by the action of potash-lime at 427° F. It is easy to understand how by this means substances may be formed which contain less carbon in their equivalent than the substance decomposed, but not how a substance containing more carbon can be produced. It is a universal observation, that in energetic decompositions by which the radical is destroyed with the organic compound, the bodies produced are never more complicated, but always more simple in their composition.

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* Chem. Gaz., vol. xiii. p. 31.

Lastly, I must observe, that Scharling may readily convince himself, as I have done, that crude æthal is a mixture, by repeatedly crystallizing from its alcoholic solution the body obtained by the saponification of spermaceti with an alcoholic solution of potash, decomposing the soap by chloride of barium, extraction of the baryta compound by alcohol and æther, and distilling off the latter, after it has been freed by boiling with muriatic acid from the baryta still contained in it, and separated from the fatty acids still present by boiling with a very dilute solution of potash and mixing with water. He will then observe a constant elevation of the melting-point of the mass deposited on cooling, especially when the quantity of alcohol employed in recrystallization is not too small.

It will be very agreeable to me if Scharling would consider it worth while to repeat his experiments with complete exclusion of air. He would then become convinced of the correctness of my observations, and acquire an additional means of establishing the nature of the train oil of the beaked whale.—Liebig's *Annalen*, xcvii. p. 271, March 1856.

On Thioformylic Acid. *By* H. Limpricht.

But few of the organic compounds derived from the type of sulphuretted hydrogen have hitherto been closely examined. As far as I am aware, these are only the hydrosulphates and sulphurets of the alcoholic radicals ($C^4 H^6 S^2$ and $C^8 H^{10} S^2$), sulphuret of carbon, sulphocyanic acid, and lastly, the thiacetic acid recently discovered by Kekulé. A compound, probably homologous with the latter, was long since observed by Wöhler[*], and at his inducement I undertook an investigation of it with M. Ritter.

In the preparation of formic acid, if dry sulphuretted hydrogen gas be passed over formiate of lead at a temperature above 212° F., the formic acid possesses an unpleasant, garlic-like odour, and not unfrequently small acicular crystals separate from it. These are obtained in the largest quantity when the decomposition of the salt is effected in a tubulated retort, heated during the operation to 392° to 472° F. The formic acid sometimes solidifies in the receiver in a short time in consequence of the separation of crystals, and the fluid filtered from it leaves almost an equal quantity of this product on distillation. If it does not become perfectly colourless after washing with cold water and drying over sulphuric acid, it may be recrystallized from hot alcohol; but for this purpose a very large quantity of alcohol is required. The amount obtained from a pound of formiate of lead is not more than a few grammes.

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[*] Liebig's Annalen, xci. p. 125.

We believe that this body may be named *thioformylic acid*, with the formula $C^2 H^2 O^2 S^2$, although in favour of this only the determination of the sulphur can be adduced. It furnished, after oxidation with nitric acid in a retort,—

C	..	..	2	=	12	19·3
H	..	..	2		2	3·2
O	..	..	2		16	25·9
S	51·2	52·5	2		32	51·6

The determinations of the carbon and hydrogen furnished no concordant results*, notwithstanding the employment of peroxide of lead.

For this composition, its formation from formic acid would be expressed by the following equation:—

$$\underset{\text{Formic acid.}}{C^2 H^2 O^4} + 2HS = \underset{\text{Thioformylic acid.}}{C^2 H^2 O^2 S^2} + 2HO.$$

Thioformylic acid crystallizes from formic acid or boiling alcohol in fine needles; it fuses at about 248° F., and sublimes even at a lower temperature in small transparent crystals. It has a weak odour of garlic, is insoluble in water, and scarcely soluble in cold alcohol or æther, but dissolves in those fluids at a boiling heat. A portion of it is volatilized with the alcoholic vapours.

Concentrated sulphuric acid dissolves thioformylic acid with the assistance of a gentle heat, with evolution of sulphurous acid and separation of sulphur; concentrated muriatic acid has no action upon it even when boiling; nitric acid easily destroys it when heated, and oxidizes the sulphur to sulphuric acid; a small quantity dissolves in boiling acetic acid, but separates again on cooling.

When thioformylic acid is heated with dilute sulphuric acid and peroxide of lead, the latter acquires a paler colour; and when it is heated with chromate of potash and dilute sulphuric acid, oxide of chrome is formed. By fusion with hydrate of potash, a reddish-yellow mass is produced; and when dilute sulphuric acid is poured over this, sulphuretted hydrogen and an odour of garlic are evolved; solution of potash dissolves only a small quantity of it even when boiling; and the solution treated with acids evolves traces of sulphuretted hydrogen. It is insoluble in sulphuret of ammonium, both when cold and at a boiling heat.

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* The combustion I. was effected with peroxide of copper; between the chloride of calcium tube and the potash apparatus a tube filled with peroxide of lead was placed. The analysis II. was made with chromate of lead, without a peroxide of lead tube; and III. with chromate of lead and a peroxide of lead tube. In the two last experiments, chromate of lead was put only into the hinder part of the tube; the anterior portion contained granulated oxide of copper. The analyses gave,—

	I.	II.	III.				
C	26·1	25·7	23·1	2	=	12	19·3
H	5·6	4·7	6·3	2		2	3·2
O	...	...	...	2		16	25·9
S	...	...	...	2		32	51·6

The alcoholic solution of thioformylic acid has no reaction upon litmus; it is not changed by perchloride of iron; gives a yellowish precipitate with acetate of lead, which becomes black when the fluid is heated; and with nitrate of silver a precipitate, which is at first white, but soon becomes black, and which dissolves partially in hot alcohol, with separation of metallic silver or sulphuret of silver. From its ready decomposability, the silver compound could not be obtained in a proper condition for analysis.—Liebig's *Annalen*, xcvii. p. 361, March 1856.

Analysis of the Cleveland Iron Ore. *By* A. Dick, Esq.

The ore was weighed after drying at 212° F.

Protoxide of iron	39·92
Peroxide of iron	3·60
Protoxide of manganese	0·95
Alumina	7·86
Lime	7·44
Magnesia	3·82
Potash	0·27
Carbonic acid	22·85
Phosphoric acid	1·86
Silica, soluble in hydrochloric acid	7·12
Sulphuric acid	trace
Bisulphide of iron (iron-pyrites)	0·11
Water in combination	2·97
Organic matter	trace
Residue, insoluble in hydrochloric acid	1·64
	100·41

Composition of the residue insoluble in hydrochloric acid:—

Silica, soluble in dilute caustic potash	0·98
Silica, insoluble in dilute caustic potash	0·52
Alumina with a trace of peroxide of iron	0·10
Titanic acid, about	0·03
Lime	trace
	1·63

The ore contains no metal precipitable by sulphuretted hydrogen from the hydrochloric acid solution.

In the residue insoluble in hydrochloric acid, minute, bright, black crystals were detected, which were proved to contain titanium, and were supposed to be anatase. Prof. Miller of Cambridge has been able to measure certain of the angles, and found them to be identical with similar angles of anatase. The discovery of this mineral in the Cleveland ore is at least a point of considerable mineralogical interest, and may possibly furnish some additional indication of the nature of the rock from which it was derived.

The silica in the insoluble residue exists, it will have been observed, in two states, about two-thirds being soluble in dilute caustic potash, and one-third insoluble in that solvent. The rounded white particles, which, according to Bowerbank, have a truly oolitic or concentric concretionary structure, are entirely formed of the soluble silica.

The silica which existed in the hydrochloric acid solution was that which was present in a state of combination in the ore, probably with both protoxide and peroxide of iron; and the peculiar greenish-grey colour of the ore was doubtless due to the presence of this silicate of the mixed oxides of iron, just as the colour of the green particles in the so-called greensand is believed to be due to the like cause.

The proportion of phosphoric acid in the ore is comparatively large, and may be easily accounted for by the fossiliferous character of the ore. The quality of the iron smelted from this ore would certainly be very sensibly affected by the proportion of phosphorus, and probably also by the silica existing in a state of combination.—*Proc. Geol. Soc.*, May 7, 1856.

On a Compound of Baryta with Alcohol.
By M. Berthelot.

In their memoir upon wood-spirit, Dumas and Peligot have described a compound of baryta with this alcohol, $BaO, C^2 H^4 O^2$. The author has obtained the corresponding compound with ordinary alcohol, namely, $BaO, C^4 H^6 O^2$.

It is produced when commercial absolute alcohol is brought in contact with anhydrous baryta, and the damp air is carefully excluded from the solution. The baryta dissolves in it; and if the fluid be filtered away in one or two days, about a thousandth part of baryta is found to be dissolved. But if a few fragments of anhydrous baryta be put into this solution, these are dissolved in eight to ten hours, and 10 cub. centims. of alcohol then contain 0·77 grm. of baryta. On the addition of a small quantity of water, an abundant precipitate is thrown down, which is soluble in pure water. If the alcoholic solution be boiled, a granular substance is deposited; this is the compound $BaO, C^4 H^6 O^2$. If the fluid in which it was formed be allowed to cool, the precipitate again dissolves.

The existence of compounds of wood-spirit and ordinary alcohol with baryta stands in agreement with other known facts. Thus potash, dissolved in alcohol, retains a portion of the latter when distilled, and this only disappears on the addition of water. Lime also holds back a portion of alcohol. From this it appears that the alcohols, like the sugars, possess the faculty of combining with alkalies.—*Ann. de Chim. et de Phys.*, 3 sér. xlvi. p. 222.

ANALYTICAL CHEMISTRY.

On the Determination of Lime for Agricultural Purposes.
By Dr. Kraut.

The author has compared with one another various methods of determining lime for agricultural purposes; he states that the one recommended by Hempel is the best when certain modifications are made in it. It is equally applicable to substances which contain but little lime, and to such as consist almost entirely of that body. The reagents required are—

1. *Dilute Nitric Acid.*—30 cub. centims. dissolve 3 to 4 grms. of carbonate of lime.

2. *Ammonia.*—When mixed with an equal volume of nitric acid, the fluid remains slightly ammoniacal.

3. *Tetroxalate of Potash.*—$\frac{1}{10}$ atom of this$=\frac{1}{5}$ atom of oxalic acid is weighed off, dissolved in water with addition of ammonia, and the solution made up to 1000 cub. centims. 1 cub. centim. of this represents 0·01 grm. of carbonate of lime.

4. *Permanganate of Potash free from Chlorine*, in a solution so diluted, that at least 1 vol. of it is necessary to convert 1 vol. of the solution of oxalic acid into carbonic acid.

5. *Concentrated Sulphuric Acid free from Nitrous Acid.*

Such a quantity of the substance to be investigated is weighed off, that 30 cub. centims. of the nitric acid above mentioned will be more than sufficient for the solution of its lime; this will be 2 to 3 grms. for substances in which the presence of lime is distinctly recognizable by their effervescence on the addition of acid. It is freed from organic substances and protoxide of iron by continued calcination with access of air, and put without loss into a glass vessel. A pipette of 30 cub. centims. is filled with the nitric acid, which is poured to the substance, the vessel lying obliquely; solution is effected by boiling, and an equal volume of ammonia is added to the hot fluid. The fluid, which is either a neutral or ammoniacal solution, is mixed with such a quantity of the solution of oxalic acid that after all the lime is precipitated oxalic acid may still remain in solution. How much will be required for this purpose may be judged approximately from the more or less strong effervescence exhibited by the substance during its solution. In every case 100 cub. centims. will suffice for 1 grm. of the substance containing lime. The precipitate is allowed to settle, the clear fluid is filtered away, and the precipitate carefully washed. The hot filtrate is mixed with sulphuric acid, and permanganate of potash is dropped into it from a burette with a glass cock until the fluid remains of a light red colour. From the quantity of permanganate of potash employed, its value with relation to oxalic acid having been previously ascertained, the amount of the latter contained in the filtrate is calculated in the usual way; and by deducting this from the entire quantity employed, we find the amount combined with lime. The strength of the oxalic acid, $\frac{1}{5}$ atom in the litre, facilitates the calculation, as each cubic centimetre represents 0·01 grm. of carbonate of lime, or 1 per cent. when 1 grm. of substance is employed.

The changes from Hempel's process in that above described are—

1. *The employment of tetroxalate of potash instead of free oxalic acid.*—This salt is preferable, because its amount of potash can be determined by simple calcination, and thus its purity and normal amount of water may be ascertained with certainty. The commercial salt is perfectly pure after one recrystallization, whilst the oxalic acid of commerce is contaminated with this very salt. As no

alkalimetric fluid is to be prepared in this case, its difficult solubility need not be taken into consideration, and is removed from the first by the addition of ammonia.

2. *The employment of permanganate of potash free from chlorine.*—It is obtained fit for the present purpose by one or two crystallizations. If ordinary permanganate of potash, which in consequence of its mode of preparation contains chloride of potassium, be employed, nitric acid is excluded as a solvent, as the chlorine which is evolved by the contact of the fluids destroys a portion of the oxalic acid. The substance under analysis must therefore be dissolved in muriatic acid, and the fluid must not be heated before the addition of the permanganate of potash. In the cold, however, the mutual action of oxalic and permanganic acids is so slow, that the analysis takes much more time than the removal of chlorine from the reagent; and, besides, operating with cold fluids, an analysis may be far more easily spoiled by an incautious addition of permanganate of potash.

As it has been repeatedly asserted that lime is but imperfectly precipitated by oxalic acid from solutions containing oxide of iron, it is always more certain to make the addition of the oxalic acid after the solution has been saturated with ammonia. The author however has not been able to convince himself of the correctness of this assertion.

The author adduces many experiments which prove that sufficiently exact results were obtained by this method, in the analysis of fluids containing a known amount of lime. The slight error of the method of determination gives the amount of lime too high.——Henneberg's *Journ. für Landwirthschaft*, 1856, p. 112.

On the Bichromate of Potash and Sulphuric Acid Test for Strychnine. By C. W. Bingley, Ph.D., F.C.S.*

When strychnine in powder is moistened with a single drop of undiluted sulphuric acid, and a small fragment of bichromate of potash is placed in the liquid, a beautiful and most intense violet tint immediately appears at the points of contact, and is speedily diffused over the whole liquid, disappearing entirely in a few minutes (*vide* Chem. Gaz., vol. x. p. 198, and *Ib.*, vol. v. p. 15), leaving the liquid coloured a deep yellow-orange colour by the bichromate of potash.

But if a considerable portion of tartarized antimony be present in solution, along with a small portion of strychnine either in solution or in powder, the violet tint is not produced, as in the case before alluded to, but a pale greenish colour, which is much more persistent, is apparent.

With the chloride of antimony, the presence of strychnine, even in a large quantity, fails entirely in producing the violet tint with the addition of sulphuric acid and bichromate of potash.

Medical Institution, Sheffield,
May 27, 1856.

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* Communicated by the Author.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Compounds of Carbon and Iron, and their Influence on the Production of Pig Iron. By A. GURLT.

THE compounds of iron with carbon, which are of such great importance in the commercial production of iron, inasmuch as, owing to the very difficult fusibility of pure iron, it would be impossible to obtain the metal without them on the large scale, belong to that class of chemical compounds in which several atoms of the electro-positive constituents are united to 1 atom of the electro-negative body; they may therefore be considered as subcarburets analogous to certain combinations of iron with sulphur. The tetracarburet, as it occurs most frequently in the white crystalline pig iron (*spiegel-eisen*) or specular iron, and the varieties related to it, has long been familiar to us from the researches of Karsten. In it the iron is completely saturated with carbon, and cannot be made to take up more by prolonged fusion with charcoal. In its pure state it consists of 94·88 parts of iron, and 5·12 carbon, corresponding to the formula $Fe^4 C$. In this compound the whole of the carbon is chemically combined with the iron; it is rarely met with however in a state of absolute purity. In general it contains, in addition to iron and carbon, a variable amount of manganese, occasionally amounting to 6 per cent. As it is most frequently obtained from ores containing much manganese, on the other hand it usually contains a rather larger amount of carbon than the pure tetracarburet. As, however, the manganese replacing the iron in this compound possesses a lower atomic weight than the iron, a certain weight of manganese will combine with a larger amount of carbon than an equal weight of iron; and the amount of carbon which may exist in it without exceeding the maximum for the pure tetracarburet, will depend on the proportion of manganese existing in the specular cast iron.

The pure tetracarburet of iron possesses a specific gravity of 7·65 to 7·66, a silver-white colour, great hardness, is very brittle, and is commonly crystalline, although its form is of very difficult determination. According to Karsten and Hausmann, it does not belong to the cubic system, but the crystals consist of oblique prisms, among which an oblique terminal plane can occasionally be discovered, so that it would rather appear to belong to the oblique system. The crystals are most frequently tabular, and then appear to be merely rudimentary, intersecting one another at indefinite angles. Mitscherlich observed an angle of 120°; Rammelsberg one of 116°, also of 130° to 131°; and the author found in a specimen from Silesia, angles belonging to oblique prisms measuring respectively 128° to 129° and 52° to 53°; still the primitive form cannot with certainty be determined from these measurements. The fracture is highly radiate crystalline, and frequently exhibits cavities between the crystalline laminæ. The specular iron is the most fusible of all the combinations of iron with carbon. Its melting-point is about 1600° C., and it becomes solid without previously assuming a thick pasty condition.

The octocarburet of iron, Fe^8C, does not appear to have been recognized hitherto, although it not unfrequently occurs crystallized in gray pig iron, never however in white pig iron. It is distinguished from the tetracarburet not only by its chemical composition, but also very distinctly by its crystalline form and its other physical properties. The crystals which were observed by Karsten, but not further examined, belong to the regular or cubic system, and almost always appear in the form of confused octohedral groups, with the planes not well defined but the angles occasionally sharp.

The author examined a piece of such crystallized cast iron from the works of Gleiwitz in Upper Silesia, found in the core of a cast-iron gun. It presented the following composition:—

Carbon	2·46
Graphite	2·84
Silicium	0·26
Iron	94·20
Sulphur Phosphorus	traces
	99·76

The absolutely pure octocarburet of iron should contain by calculation 2·63 carbon, and 97·37 iron. In the above specimen, however, a small portion of the chemically-combined carbon was replaced, as has often been observed to be the case, by a small portion of silicium, while the graphite must be considered as mechanically mixed with the iron.

Hence the crystals examined may be considered as a mixture of a carburet of iron and siliciuret of iron, consisting of—

$$\begin{aligned} 91{\cdot}548 \text{ per cent. Fe} + 2{\cdot}46\text{ C} &= 94{\cdot}008\ Fe^8C \\ 2{\cdot}660 \text{ per cent. Fe} + 0{\cdot}26\text{ Si} &= 2{\cdot}920\ Fe^8Si \\ \text{Graphite} &= \underline{2{\cdot}840} \\ & \ 99{\cdot}768 \end{aligned}$$

In the former constituent the carbon is to the iron as 1 : 37·3, and in the latter the silicium is in the proportion of 1 : 10·0, closely agreeing with the calculated composition; and as the octocarburet so largely preponderates in this compound, one is fully justified in describing it as such.

The physical properties of the octocarburet are very different from those of the tetracarburet or specular iron; the specific gravity is =7·15, the colour iron-gray, the hardness and brittleness much inferior; the former is to a certain degree malleable, as it retains the impression of the hammer when struck, while the latter flies to pieces; the fusibility of the octocarburet is less than that of the specular iron. It appears to occur frequently, its production being invariably connected with that of gray iron. The crystals are commonly found in the form of pyramids, extending to as much as two lines in thickness, often beautifully iridescent on the surfaces, in the cavities of large castings such as rolls and pieces of ordnance. These crystals, however, are not to be confounded with those regular crystals of soft malleable iron, which are sometimes produced during the oxidizing melting processes, such as refining and puddling; these latter contain no carbon, and are so free from foreign matters that they may be considered as nearly chemically pure iron.

The author believes that similar crystals to those of the octocarburet described above have been found at the blast-furnaces at the Königshutte in Upper Silesia, Ilsenberg in the Hartz, Marienhutte near Zwickau, &c., which have most probably a similar composition; but he has had no opportunity of investigating them more accurately.

As the existence of two distinct subcarburets of iron may be taken as a fact, it will become important to inquire what influence they exert on the production of pig iron. The several varieties of cast iron which are technically received at the iron works may be brought into two groups, which differ from each other chiefly in their physical qualities. The first group will include all the varieties of white cast iron, which exhibit a silver-white colour on the fracture, and a more or less radiate crystalline structure, together with a great degree of hardness and brittleness, and also a relatively high specific gravity=7·2 to 7·6; and in them no graphite is ever to be distinguished by the naked eye. This group must however be subdivided into two subdivisions, determined by their chemical composition, the first of which will include all those varieties of white cast iron containing a large amount of chemically-combined carbon, amounting to from 4 to 5 per cent., such as specular iron and varieties allied to it. The second subdivision includes all the descriptions of white cast iron containing smaller quantities of carbon, included in the technical term "white cast iron," but which generally contain considerable quantities of sulphur and phosphorus. In the second larger group are included all the varieties of gray cast iron in which graphite can be distinguished by the naked eye, possessing a specific gravity of 7 to 7·2, a granular structure, gray colour, and greater toughness, but a less degree of hardness than the varieties of the first group. The gray cast iron must also be separated into two subdivisions, of which the mottled cast iron is the richer in carbon; the other is the gray pig iron proper, containing frequently a considerable amount of silicium. The essential constituents of all pig iron are but two, viz. iron and carbon, the latter in its modifications of graphite and chemically-combined carbon; all the other substances occurring in it may be considered as impurities. Among the electro-positive bodies, manganese is almost always present in cast iron, and at times zinc and copper, which replace an equivalent proportion of the iron; while the electro-negative substances, as sulphur, phosphorus, and silicium, replace the carbon combined with the iron. In proportion to the quantities in which these impurities are present is their effect in modifying the physical qualities of the metal, such as its toughness and specific gravity.

Hitherto these impurities in the cast iron, which seldom amount to more than 4 per cent., have been neglected in considering its chemical constitution, although Karsten has directed attention to the influence which the electro-negative impurities exercise on the compounds of iron and carbon on fusion. As his experiments throw so much light on the formation of the carburets of iron, it may not be considered out of place here briefly to describe his results.

Karsten found that when cast iron containing the largest amount of chemically-combined carbon, $Fe^4 C$, was melted with sulphur in a covered clay crucible, there was found, on cooling, on the surface sulphuret of iron, under this a layer of separated carbon in the form of graphite, and under this again a mass of cast iron with the maximum of carbon, proving in a most striking manner that the chemically-combined carbon is separated at the temperature of fusion in the form of graphite from its combination with the iron, and on the other hand that carbon was incapable of decomposing the sulphuret of iron. When this experiment was varied by pouring melted gray cast iron containing only 3·93 per cent. of carbon (of which 3·311 was graphite, and 0·625 chemically combined) on to sulphur whose quantity was not sufficient to convert all the iron into sulphuret, or when gray cast iron was melted with sulphur, there was found under the stratum of sulphuret of iron white cast iron with maximum of carbon, the whole of which was chemically combined with the iron; and when the amount of sulphur was slightly increased, graphite was also separated. From which it is clearly proved, that the carbon in the melted cast iron, on the addition of sulphur, is continually concentrating in that part of the iron not combined with the sulphur until the point of saturation is reached, when graphite begins to be separated.

In strict analogy to that of sulphur is the action of phosphorus, and also of silicium, which form phosphuret and siliciuret of iron, while the carbon is concentrated in the remaining iron, or the excess separates in the form of graphite. This behaviour of the electronegative constituents of the cast iron will explain the occasional occurrence of graphite in white cast iron, and even in well-characterized specular iron; and this appearance is usually to be attributed to the presence of a little silicium, which combines with the iron at a very high temperature, and decomposes a portion of the carburet of iron. In fact, a small portion of silicium is always found in the analyses of white cast iron with graphite. The uncombined carbon however exists in such small proportion in white cast iron as not to be seen by the eye, but is only discovered in its chemical analysis. From the action of sulphur, phosphorus, and silicium on the carburets of iron above described, it follows that they must be considered as chemically combined with the iron, replacing the carbon chemically combined with it.

It is well known that the absolute quantities of carbon are different in white and gray pig iron, even when they are prepared from the same ores and under similar circumstances, the proportion of carbon being always less in the gray than in the white cast iron. The only exceptions to this rule are the varieties of iron produced by remelting in a reverberatory furnace, by which white cast iron can be converted into gray, and *vice versâ*. In such irons the altered product usually contains the same amount of carbon as the material employed originally contained, one portion of the carbon merely passing from one modification to the other, viz. from the state of chemically-combined carbon to that of graphite when the product is gray, or from graphite to chemically-combined carbon when the product is white. In gray pig iron a large proportion of its carbon is not in a state of chemical combination, that is to say, it is in the form of graphite; with white cast iron this is very rarely the case, and in those rare cases existing in very minute degree. It was mentioned above, that the conversion of the chemically-combined carbon into graphite was effected by the decomposition of the tetracarburet by sulphur, silicium, and phosphorus; there is, however, another method of separating the carbon from the tetracarburet in the form of graphite, that is, by heat.

It is known from experience that white pig iron may be converted into gray, causing a separation of carbon in the form of graphite, by exposing it to a degree of heat much above that required to effect its fusion; specular iron may even be converted into gray cast iron in this way; now this can only take place when its composition as tetracarburet is destroyed, and it passes to some lower degree of carburation, setting free carbon as graphite. This high degree of temperature therefore effects this decomposition of the tetracarburet, and slow cooling favours the separation in large flakes; but even when this cooling is rapidly effected, the pig iron contains an equal quantity of graphite, which may be determined by chemical analysis, but which is difficult to be detected by the eye from its being disseminated in minute particles throughout the mass, and for this reason a gray cast iron rapidly cooled appears to the eye like white cast iron. The degree of heat above that of its fusing-point necessary to convert completely the specular iron into gray iron has not been ascertained with accuracy, owing to the difficulty of measuring such high degrees of temperature; so much experience has taught, however, that in order to obtain gray pig iron, the temperature of the furnace must range far above the fusing-point of specular iron.

As the absolute, as well as the relative quantity of carbon in the several varieties of cast iron is different, it may be asked whether it exists in any definite proportion to the iron not combined with any other electro-negative substance. With regard to white cast iron, the view is held that the combined carbon is united to the whole mass of the iron, though not in definite proportions. With regard to gray cast iron, however, it has been assumed that only a proportionately small quantity of the iron was chemically united to the carbon, forming a carburet, which was held in solution as it were in the remainder of the iron which existed in the state of malleable iron; still this soft iron was not to be considered altogether free from carbon, but to contain a minute quantity combined with it in the same manner as in bar iron. Against this view, which even yet has many supporters, it may be urged, that although it certainly is possible for carburetted iron to dissolve soft iron, as in the natural steel refinery and in the fabrication of cast steel, still the product is steel and not pig iron, and that its production depends upon processes essentially differing in principle from those upon which the production of pig iron depends. Steel is produced under all circumstances, directly or indirectly, by an oxidizing melting process, in which the separation of the sulphur, phosphorus, silicium, and also both the chemically-combined and free carbon, is so far effected by the oxygen of the air, that only a portion of the iron remains in the state of carburet, while the whole remaining mass is in the condition of soft iron. In the production of pig iron exactly the reverse occurs; the melting process is a reducing one, in which the iron is exposed to the action of a large excess of carbon and carburetted gases in the most intimate contact. If it be now considered that the affinity of iron for carbon at high temperatures is very powerful, as the process of cementation sufficiently proves, it must necessarily be admitted that if by any chance soft malleable iron should be present in gray pig iron, it must necessarily unite with carbon to pass again into a combination of iron and carbon, for it is impossible it could exist uncombined under the influence of the reducing gases of the furnace in the presence of the graphite, always intimately mixed with the gray iron.

While therefore we are forced to admit that the iron never exists in pig iron in the condition of malleable iron, but must always be, throughout its whole mass, in a state of combination with the electro-negative constituents, as carbon, sulphur, phosphorus, and silicium, the hypothesis of the existence of a polycarburet, which Karsten and Berthier assumed in order to account for the peculiar properties of crude iron, and which, according to Berthier, would contain 18·3 per cent. of carbon, must fall to the ground, because such a polycarburet could only exist simultaneously with soft iron. But independently of this reason, the hypothesis of a polycarburet is upset by the simple fact, that iron, by taking up rather less than 6 per cent. of carbon, is already saturated; and therefore its combination with 18 per cent. is an impossibility. We may therefore consider it as proved, that the chemically-combined carbon is chemically united to the whole mass of the iron not already combined with the other electro-negative substances, and that the graphite is the only mechanical admixture in pig iron. If we are no longer permitted to doubt the existence in every description of pig iron of certain definite carburets, it becomes important to know the combining proportions of the carburets from which these different varieties of cast iron have originated.

In the specular iron, the pig iron containing the largest amount of carbon, these proportions are known: they are those of the tetracarburet, which contains 1 atom of carbon to 4 of iron. With regard to the gray cast iron, it is certainly remarkable that the crystalline octocarburet described above should occur so frequently and exclusively in it; and it becomes important to seek herein a close relation between the gray cast iron and the octocarburet. In fact, the following reasons appear to warrant the conclusion, that the carburet of iron existing in gray cast iron is the octocarburet:—1st, the physical properties, as colour, hardness, toughness, specific gravity, malleability, agree in both; 2ndly, the octocarburet occurs very frequently in gray cast iron, and separates in the crystalline form from gray cast iron only; 3rdly, the tetracarburet (specular iron), at a temperature much above its melting-point, becomes converted completely into gray cast iron, in which the proportion of chemically-combined carbon represents that of the octocarburet.

If therefore we are authorized in considering the carburet of gray cast iron as identical with the octocarburet, and we bear in mind that gray cast iron is produced by the decomposition of $Fe^4 C$ at an elevated temperature, it becomes exceedingly probable that gray cast iron is always formed from the tetracarburet. If now the decomposition of the $Fe^4 C$ should not be complete, owing to the necessary temperature not being sufficiently protracted, it is clear that a cast iron will be produced composed of a mixture of tetra- and octocarburet, such as the mottled cast iron. Mixtures of octo- and tetracarburets of iron are found, however, in other cast irons differing much from the above, and which contain a large amount of white cast iron poor in carbon. This white pig iron, which often contains much sulphur and phosphorus, is always produced at a proportionately lower temperature and with an overcharged furnace. The small quantity of fuel consumed in the reduction of the iron produces this effect: the reduced iron does not remain long enough in contact with the fuel, and the supply of carbonizing gases being deficient, it does not become thoroughly saturated with carbon, and a portion of the iron remains as octocarburet, and is mixed with that portion which has been saturated with carbon to form the tetracarburet.

[To be continued.]

On the Manufacture of the Superphosphates. By Dr. A. Müller.

Long as bones have been employed as manure, and long as their difficult decomposability in the fresh state has been known, it is but recently that general endeavours have been made to secure a higher and quicker return from the bones by a preliminary treatment. All that was done at first was to crush the bones coarsely; afterwards the assistance of a previous fermentation to destroy the toughness of the cartilage was employed; and then various forms of mills were made use of with a view to a more complete crushing of the material. In the present day sulphated bone-dust and the fine bone-dust from steamed bones dispute for the preference, and both are undoubtedly better than the earlier bone-dusts. Both, when well prepared, contain a great abundance of fertilizing ingredients, and both are in a state of extremely fine division, in which they may be immediately assimilated by the plants; when equally well prepared, one is only to be preferred to the other upon considerations of cost.

Chemistry has little to do with the preparation of the steamed bone-dust; the steaming is a simple process, requiring no chemical knowledge, and several analyses have shown that during their steaming the bones principally lose fat and but little gelatine. Although it is placed beyond a doubt, by numerous observations of practical agriculturists, that steamed bone-dust is assimilated by plants in a tolerably short time, the sulphated bone-dust still deserves the fullest consideration, especially until the manufacturers of the former manure can prepare it in sufficient quantity for the general requirements, and more easily soluble than the sulphated material.

A chemical preparation of the bones by treatment with sulphuric acid furnishes a manure that must be preferred to the steamed bone-dust, because the phosphate of lime contained in the bones is converted into a more soluble compound, and at the same time a mechanical disintegration of the bony tissue takes place.

Unfortunately these good qualities are scarcely to be met with in most of the samples of sulphated bone-dust which occur in commerce, for either only the finer parts of a coarse bone-dust are converted into superphosphate, whilst the coarser fragments, as might be expected, have escaped the action of the acid, or the whole mass of bone-dust is indeed penetrated by an excess of acid; but the acid phosphate has again been converted into the neutral salt by slaked lime or soap-boilers' refuse, so that a considerable sum is paid for a mechanical division, with the addition of a considerable weight of useless matter. There is less to be said against those manufacturers who dry the acid bone-mass with coal-dust or peat-charcoal, and thus render it pulverizable, although they not only use a considerable quantity of sulphuric acid, but also dilute their manure, and thus increase its weight too much for distant transport. The best process yet employed consists certainly in kneading the bone-paste, prepared with an excess of sulphuric acid, with bone-charcoal, which would otherwise be incapable of employment, and drying the mass; of course, however, a product of this kind can only be prepared by a few manufacturers, and cannot be brought into market in anything like sufficient quantities. Its manufacture is confined to the districts of the sugar-refiners.

The following method is free from this limitation, and at least equally favourable in its results; the author recommends it from his own experience.

As the complete solution of 155 parts of phosphate of lime [$(CaO)^3, PO^5$] requires 98 parts of hydrated sulphuric acid (SO^3, HO), about 104 parts of English sulphuric acid, containing a little water or about 90 parts of fuming sulphuric acid, but the bones, including the shafts, articulations, and cartilages, give on an average 55 to 60 per cent. of ashes containing 50 per cent. of phosphate of lime, we may calculate that for the breaking up 100 kilogrms. of bone-dust (taking into account the carbonate of lime) the quantity of ordinary English sulphuric acid required cannot exceed 36 kilogrms. Many English manufacturers use as much as 50 per cent. of sulphuric acid to the bone-dust; but this quantity is excessive, and needlessly increases the price of the manure. Less acid even may be used by confining its action to the coarser fragments of the bone-dust, as these will longest resist solution in the soil.

By the ordinary process the very reverse takes place; the whole of the bone-dust to be prepared is treated at once, or by degrees, with sulphuric acid, and the minute particles are first converted into superphosphate, the other portions following in proportion to their size, the largest fragments remaining untouched. The author therefore recommends the separation of the dust from the bone-mills by means of three or more sieves into dust, the particles of which are under 1, 2, or 3 millims., &c. The coarsest fragments are then first treated with the whole of the sulphuric acid, and the other portions are added in the order of their increasing fineness.

The calculation of the quantity of sulphuric acid to be employed in this case has nothing to do with the entire quantity of the bone-dust, but only with the portions which require disintegration, such as the fragments whose smallest diameter is above 2 millims.; the particles passing through apertures of 1 millim. certainly do not require it; the intermediate portions according to circumstances. If 40 kilogrms. of the coarsest fragments have been sifted out of 100 kilogrms. of bone-dust, they certainly only require 15 kilogrms. of English sulphuric acid, and if 25 kilogrms. be employed, there remains an excess of acid sufficient for 26 kilogrms. of finer fragments.

The sulphuric acid requires an addition of water, as English sulphuric acid contains only 20 per cent. of water; and not only is water lost during the operation, but 155 parts of phosphate of lime fix at least 20 parts of water in their conversion into superphosphate, and the 136 parts of sulphate of lime formed at the same time may fix 36 parts of water. Nearly half its weight of water may therefore be added to the sulphuric acid.

It is advisable only to add the water after the coarsest fragments are soaked with the sulphuric acid, and to pour it in in small portions with constant stirring, as in this way the heat evolved by the mixture is favourable to the operation. The application of heat is unnecessary, and after standing for twenty-four hours the fragments of bone are completely softened, and may be crushed with the fingers. The finer particles are now kneaded into the paste, which is left standing for some days before the addition of the fine dust, after which, by leaving the mass in a dry place, the moisture soon disappears. An increase in the quantity of water facilitates the kneading of the mass, when the arrangements of a manufactory are such that hot drying places may be made use of.

By the treatment of 100 kilogrms. of bone-dust in the above manner with 25 kilogrms. of English sulphuric acid and 13 kilogrms. of water, about 130 kilogrms. of superphosphate of lime are produced. This is certainly dearer than the same weight of the ordinary sulphated bone-dust, but possesses the same efficacy as 200 to 300 kilogrms. of the latter, and is therefore comparatively cheaper, without taking into consideration the greater facility of transport.

In external appearance the preparation is a whitish-gray, crumbly, or pulverulent mass; in dry air it does not become moist, its taste is scarcely perceptibly acid, and it may therefore very well be kept in sacks.

The advantages of the process just described over those already in use are, that—

1. The acid acts most powerfully upon the portion which is most difficult of solution;

2. Only a very small quantity of sulphuric acid is required; and

3. The unnecessary increase of weight is avoided, and distant transport is thus facilitated.—Henneberg's *Journ. für Landwirthschaft*, 1856, p. 107.

PROCEEDINGS OF SOCIETIES.

Royal Institution.

April 4, 1856.—"On the Measurement of the Chemical Action of Light." By Henry E. Roscoe, Esq., B.A., Ph.D.

No attempt has been made, up to the present time, accurately to measure the changes brought about in chemical substances by the action of the solar rays.

The peculiar action of light on chemical bodies was first observed by Scheele on chloride of silver. Since that time the subject of the chemical action of light has attracted a large amount of attention, as the present perfection of the arts of the daguerreotypist and photographer fully testify. Although we possess so many facts concerning the chemical action of light, this branch of science has only as yet arrived at that first or qualitative stage of development, through which every science must pass. The laws which regulate these phænomena are unknown to us, and we possess no means of accurately measuring the amount of the decomposition effected by the light.

The speaker proceeded to describe the results of a series of experiments carried on by him in conjunction with Professor Bunsen, which had for their object,—

1. To determine the laws which regulate the chemical action of light;
2. To obtain a measure for the chemically active rays.

When aqueous solutions of chlorine, bromine, or iodine are exposed (under certain conditions) to the direct solar rays they are decomposed, the corresponding hydracid being formed, and the oxygen of the water liberated. The difference between the amounts of free chlorine, bromine, or iodine, contained in the liquid before and after exposure to light, gives the quantity of the substance decomposed during the isolation. Now it was found that this quantity of chlorine, bromine, or iodine which disappeared, was not proportional to the time of exposure to the light; in twice the time, for instance, less than twice as much substance was decomposed. The relation between the amount of light and the amount of decomposition was found in this case not to be a simple one.

This anomalous action may be explained even from a theoretical point of view. Chemical affinity is the resultant of all the forces which come into play during the reaction; hence it is not only the interchanging atoms which influence the result, but also those atoms which, without taking part in the decomposition, surround those actively engaged. The so-called catalytic phænomena show this action in a striking manner. To apply this general principle to the special case before us; we have to begin with pure chlorine water; after the first action of the light, however, hydrochloric acid is formed, hence the composition of the solution is altered, and a different result must be expected. This theoretical conclusion was verified by experiment. Chlorine water, to which 10 per cent. of hydrochloric acid was added, did not suffer any decomposition by an exposure of six hours to the direct sunlight; during which time the same chlorine water, without previous addition of hydrochloric acid, lost nearly all the free chlorine which it contained*.

In order then to obtain a true measure of the action of light on any chemical substance, it is necessary that the body formed by the decomposition should be removed from the sphere of action. This cannot be done with chlorine water; a new sensitive substance was therefore employed.

Equal volumes of chlorine and hydrogen gases when exposed to the direct sun-light unite with explosion; in diffuse light, the action proceeds gradually. In presence of water the hydrochloric acid formed by the combination is immediately absorbed, and thus withdrawn from the sphere of action, and the diminution of the volume of the mixed gases arising from this absorption gives an exact measure of the amount of action effected by the light. The diminution in volume of the gas measured by the rise of water in a graduated tube was found to be regular, proving *that when the light is constant the amount of action is directly proportional to the time of exposure.*

The relation between the amount of action and the amount of light was experimentally determined, by allowing known quantities of diffuse light to fall upon the sensitive gas. Experiments thus conducted showed *that the amount of action is directly proportional to the amount or intensity of the light.* These simple relations were observed by Dr. Draper, of New York, in 1843, but his method of experimenting differed essentially from that employed in these researches, and was not susceptible of any very great degree of accuracy. The relation between the amount of action and the mass of the sensitive gas has not as yet been fully determined; experiment has however already shown that the relation is not a simple one.

Many very interesting phænomena were observed in the course of these investigations. When the gas is first exposed to the light no action whatever is observed; after a short time the absorption slowly begins, and increases until a maximum has been attained, after which it proceeds regularly. This phænomenon of induction probably depends on a peculiar allotropic change which the chlorine must undergo before it is capable of uniting with the hydrogen.

The speaker concluded by expressing his intention of continuing these experiments at Heidelberg, in order exactly to determine the relation which exists between the amount of action and the volume of gas employed; to investigate the phænomenon of induction; and to obtain, if possible, an absolute measure for the chemical rays.

* Poggendorff's Annalen, xcvi. 373; and Quarterly Journal of Chemical Society, Oct. 1855.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Essential Oil contained in the Alcohol of Madder.

By F. Jeanjean.

For several years an alcohol has been obtained in the South of France in considerable quantities, by the fermentation of the saccharine matters contained in the root of the madder. The alcohol thus obtained always possesses a very disagreeable and characteristic odour, and the author has examined it to ascertain the nature of the foreign bodies contained in it.

The products obtained by him formed a liquid of less density than water, and after some time deposited crystalline lamellæ. When distilled, it furnished liquid products up to 446° F., but afterwards a solid white matter was deposited in the neck of the retort. If the distillation be arrested at this point, the belly of the retort becomes filled with crystals presenting the appearance of the fronds of ferns.

From the indications of the thermometer immersed in the boiling liquid, the author suspected the presence of propionic and butyric alcohols in the first products of the distillation; the stoppage of the thermometer at 266° F. indicated the probable presence of amylic alcohol, and the products boiling at this temperature being in larger quantity than the preceding, he was enabled to analyse them, when he found them to agree in composition with amylic alcohol.

The solid matter passing at 446° F., when pressed between paper, washed in a large quantity of water, and purified by repeated crystallization from æther, forms a white powder, of a peppery odour, which however resembles that of ordinary camphor. Its analysis gave—

	I.	II.
C	77·7	77·82
H	12·2	11·9
O	10·1	10·28

corresponding with $C^{20}H^{18}O^2$, the formula of Bornean camphor.

This substance possesses a hot burning taste, and when sublimed forms small hexagonal prisms. It gives rise to the gyratory movements of camphor when thrown upon water; it is but slightly soluble in water, but very soluble in ordinary acetic acid, and in alcohol and æther, from which it is thrown down by water. Distilled over chloride of zinc or anhydrous phosphoric acid, it gives origin to a hydrocarbon, the odour of which resembles at once those of the essential oils of citron and bergamotte. Lastly, it is converted into ordinary camphor by the action of boiling nitric acid, as was observed by M. Pelouze to be the case with the camphor obtained from *Dryobalanops camphora.*

The crystals which are deposited naturally in the crude material possessing all the properties of those obtained by distillation, the author concluded that their formation was due to the hydratation of a pre-existent hydrocarbon. To isolate this, he took the liquid which passed above 284° F. in the first distillation, digested it over potash and chloride of calcium, and distilled it several times to free it from the camphor which it had carried over; it formed a liquid boiling at 320° F., with an odour like that of the essence of madder. Its analysis gave—

C	88·23
H	11·81

and the density of its vapour being 4·85, its formula is $C^{20} H^{16}$, corresponding with 4 vols. of vapour. This hydrocarbon therefore corresponds with that of Bornean camphor, and like it will be isomerous with turpentine.

The quantity of the hydrocarbon was insufficient for the determination of its behaviour towards polarized light. The camphor deviated the plane of polarization to the left. A solution of 20 grms. of camphor in 100 cub. centims. of alcohol giving a deviation of 12 degrees, the author concludes from Biot's formula that the rotatory power of this camphor for a length of 100 millims. is

$$[\alpha] = -34·5.$$

Comptes Rendus, May 5, 1856, p. 857.

On the Precipitation of Protochloride of Antimony by Water.

By M. E. Baudrimont.

Protochloride of antimony, when exposed to the air, deliquesces without decomposition; and if a certain quantity of water be added to it in this state, it gives an abundant white precipitate, known by the name of *powder of Algaroth.* In this case the water decomposes the protochloride of antimony into a precipitate of hydrated oxychloride of that metal, and muriatic acid which remains in the liquid. The powder of Algaroth may be redissolved in the same liquid in which it was formed by the addition of a little muriatic acid, and the precipitate may be reproduced by a fresh addition of water. The author has repeated this experiment twenty times upon the same portion of protochloride of antimony, but at each operation it was necessary to increase the quantity of liquid employed.

The explanation given by the author of these curious reactions is as follows:—Protoxide of antimony is one of those compounds placed at the extreme limit of acids and bases, the parts of which it can assume by turns. In presence of muriatic acid it will exert a property in antagonism with the latter, and will be basic. In the presence of water, on the contrary, it will change its part, and become acid in relation to this, which will act as a base. Now the acidity or basicity of Sb^2O^3 will depend on the proportions of water or muriatic acid which it encounters. When the acid predominates, it will become basic; by making the water predominate, Sb^2O^3 will be converted into an acid. A new addition of ClH will again change the office of Sb^2O^3, and so on.

A mixture of 100 parts of water and 15 parts of muriatic acid with 16 equivs. of water will keep protochloride of antimony in a solution which is on the brink of precipitation; the addition of a drop of water whitens it, and a drop of acid restores its limpidity. These proportions of water and acid are therefore, as it were, the measure of their respective forces as chemical agents.—*Comptes Rendus*, May 5, 1856, p. 863.

On the Production of Fluorescence by the Flame of Sulphuretted Hydrogen. *By* MM. VON BABO *and* MÜLLER.

In most flames red and yellow are predominant, and their chemical action and power of producing fluorescence are in consequence very inconsiderable. Von Babo had previously observed that the flame of sulphuretted hydrogen had a strong photographic action, and this induced the authors to employ it also in experiments on fluorescence.

A solution of quinine, exposed to the rays of this light, exhibited a very strong fluorescence; the surface of an ætherial solution of chlorophyll (obtained from ivy) appeared of a beautiful red colour; different varieties of fluor-spar, illuminated by the flame of sulphuretted hydrogen, diffused a splendid blue light, which was most beautiful in the green and violet crystals of fluor-spar from Derbyshire, but was exhibited also by other varieties, although in a far weaker degree. But the most beautiful and astonishing appearance was presented by uranium glass. A seal made out of this substance diffused a soft green light, as though it were itself luminous or phosphorescent.

This peculiar magical effect may be easily explained, when we consider that the diffused light given off by the uranium glass consists for the most part of rays which could produce no luminous action before their contact with the fluorescent substance, rays which were only rendered visible by the uranium glass, and the luminosity of which became remarkably strong in opposition to the weak light proceeding directly from the flame.

The diffused green light exhibited by uranium glass when the rays of the sun are allowed to fall upon it, is certainly more intense than that perceived with the flame of sulphuretted hydrogen; but the daylight surrounding it prevents it from making so strong an impression, so that it does not acquire the magical phosphorescent appearance above mentioned.

The rays of the sulphuretted hydrogen flame concentrated by lenses upon fluorescent bodies also produce the phænomenon of coloured pencils of light, which may be particularly well observed in uranium glass and chlorophyll.

From these observations it appeared interesting to analyse the light of the flame by means of the prism. A slit, 0·75 millim. in width, was for this purpose placed before the flame, and this was looked at through a flint-glass prism from a distance of about 12 feet. A perfect spectrum was exhibited, in which, however, as was to be expected, the violet end was unusually intense. Black lines were wanting; but, on the other hand, there were three paler lines, two in the yellow and one in the green. The palest was one of the lines in the yellow, and that in the green was next; the second line in the yellow was rather weak.

For the prism employed, the following values of the exponents of refraction were obtained for the pale lines by the assistance of the theodolite:—

The pale line in the yellow	1·6166
The weak line in the yellow	1·6178
The line in the green	1·6250

To determine exactly the position of these lines in the spectrum, the exponents of refraction of the most important lines of Fraunhofer must be determined for the same prism, which will be done as soon as the time of the year will allow of the experiments being made.—*Berichte der Verhandl. für Beförderung der Naturwissenschaften zu Freiburg*, Heft 1, 1855.

On the Action of Hydriodic Acid upon Silver.
By H. SAINTE-CLAIRE DEVILLE.

It appears to me that the place occupied by silver amongst the noble metals in the classification of M. Thenard must be changed, notwithstanding the property of being reducible at a low temperature which is possessed by its oxide. In support of my opinion, I shall in the first place adduce the curious observation of M. Regnault[*], according to which silver decomposes water at a rather low temperature: in this case it absorbs the oxygen of the water, to produce that unstable combination to which the phænomenon of spirting must be attributed. It is difficult indeed to prove that the temperature of the dissociation or spontaneous decomposition of water is higher than that required by M. Regnault's experiment, and that the oxygen is not free at the moment when the silver takes it up. But some researches which I have commenced for the approximative settlement of the temperature of the dissociation of water and some important chemical bodies, lead me to think that it is the silver alone that determines the separation of water into its elements, of which one, the oxygen, is employed in the formation of an oxide of silver. The latter, like the suboxide of copper, dissolves in the bath of metallic silver to form a sort of *rosette*, which becomes disintegrated at the moment of spirting.

These considerations would tend to the approximation of silver to tin and lead. The following is a new fact, which, I believe, has not been observed, and which leads to the same conclusion. Hydriodic acid*, dissolved in water, attacks silver with extraordinary energy, with production of hydrogen; so that in operating in a glass tube with laminated silver and concentrated acid, the liquid becomes heated and may escape from the vessel, in consequence of the abundant evolution of hydrogen gas. In the cold, the action nearly stops when the acid is saturated with silver, but recommences as soon as heat is applied; and on cooling it, a colourless salt, crystallizing in broad laminæ similar to nitrate of silver, is obtained. This salt being very alterable, cannot be separated from the liquid with which it is impregnated. It is, I think, a hydriodate of iodide of silver. The liquid which has furnished these crystals, when left to itself in the air, deposits rather large, regular, hexagonal prisms, bounded by faces which modify the horizontal angles of the prism. Thus we have the form of native iodide of silver with all its faces, as described by M. Descloiseaux†, and which that mineralogist has recognized in my specimens. Analysed by M. Appert, one of my pupils, by the elegant process applied by M. Damour to the Chilian iodide of silver‡, this substance gave the formula AgI. Thus it is exactly identical with the native iodide of silver.

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[*] Ann. de Chim. et de Phys., lxii. p. 367.

Palladium, like silver, is attacked by hydriodic acid, with evolution of hydrogen, which is weak certainly, but easily detected, and the solution of the metal takes place very slowly. Gold and platinum do not evolve a sensible amount of hydrogen, although in time they dissolve in hydriodic acid; but all the common metals that I have tried are dissolved with remarkable energy by this acid. The iodide of lead thus formed crystallizes in a singular manner.

I shall return hereafter to the curious circumstances which accompany the solution of silver in hydrobromic and hydrochloric acids. For the present I shall confine myself to concluding from the facts contained in this note, that henceforth silver must be classed beside mercury, or even beside lead, the compounds of which have a great many resemblances with those of silver.—*Comptes Rendus*, May 12, 1856, p. 894.

On the Behaviour of Chloroform to other Bodies, and especially to Ammonia. *By* Prof. HEINTZ.

1. Sodium may be heated to 392° F. with chloroform in a closed tube without producing any decomposition.

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* To prepare more than a kilogramme of hydriodic acid, which I employed in my experiments with ease and safety, I had recourse to the process described by me in the 'Ann. de Chim. et de Phys.' (lxxv. p. 46). The most convenient apparatus is a small ground tubulated retort, to the neck of which a curved tube is fixed to avoid all contact between the acid and the cork. A little water is first put into it, and then successively phosphorus and an excess of iodine, until the required quantity of hydriodic acid is produced.

† See Domeyko, Ann. des Mines, vi. p. 158; and Descloiseaux, Ann. de Chim. et de Phys., xl.

‡ Ann. des Mines, iv. p. 329.

2. Formiate of lead has no action upon chloroform at a temperature at which it would remain without decomposition in the absence of the latter.

3. At a temperature of 374° F., with exclusion of oxygen, formiate of lead is decomposed into lead, carbonic acid, and hydrogen, in accordance with the formula $C^2HO^3+PbO=2CO^2+H+Pb$.

4. Under the influence of dry ammoniacal gas, the vapour of chloroform is only decomposed at a temperature near red heat. Chloride and cyanide of ammonium are produced. But if the temperature be raised too high, a brown substance is deposited in the glass tube; this is doubtless paracyanogen, formed from the cyanide of ammonium.

5. When the aqueous solution of ammonia is long heated with chloroform to 302° F., no cyanide of ammonium is formed, but only formiate of ammonia with chloride of ammonium.

6. If a solution of ammonia in anhydrous alcohol mixed with chloroform be exposed for a long time to a temperature of 356° to 374° F., some formiate of ammonia may be formed, together with much cyanide of ammonium. Sometimes, however, neither the one nor the other could be discovered, and then a large quantity of a brown substance was formed, which contained carbon and nitrogen in large quantity, and no doubt consisted essentially of paracyanogen.

7. In this case, moreover, a larger or smaller quantity of æthylamine is produced, the formation of which however is caused only by the presence of alcohol and ammonia, and has nothing to do with the chloroform.—*Bericht. der Akad. der Wiss. zu Berlin*, 1856, p. 161.

On the Presence of Vivianite in Human Bones. By J. Nicklès.

In the cemetery at Eumont, a village in the department of La Meurthe, the earth of which is very ferruginous, there has been found among the bones, the accumulation of several centuries, two arm-bones of a female, a cubitus and a radius, having a deep bluish-green colour. One of these bones having been broken through curiosity, it was discovered that the colour was general through its whole thickness. This bone having been sent me, I have observed the following facts.

The colour was decidedly greenish; but as the osseous paste was yellow, it was evident that the colouring matter was blue. By dissolving a fragment in hydrochloric acid and supersaturating with ammonia, a white precipitate of phosphate of lime slightly bluish in tinge was obtained, showing that the colour was not due to copper. Reagents indicated the presence of iron; but as the bones all contained iron, it was not at first easy to ascertain whether this metal was in the colouring matter, although it much resembled phosphate of iron. My subsequent investigations proved that this last was true. On examining the medullary cavity with a lens, I found among the sinuosities left by the hardened marrow, brilliant points which were distinctly crystalline. With a miscroscope they were found to be rhomboidal prisms apparently oblique, some of them surmounted with a horizontal prism, and others with octohedral planes having the terminal planes applied to the two extremities of the macrodiagonal. They were too small for measurement; but by chemical methods they were found to have all the characters of phosphate of iron. Calcined with bicarbonate of soda, the acid and oxide were readily separated; and on treating the calcined product with distilled water, I obtained a residue of oxide of iron and an alkaline solution, which latter, on neutralization, afforded an abundant precipitate with ammonia, hydrochlorate of ammonia, and sulphate of magnesia. This was therefore phosphoric acid, and the substance a crystalline phosphate of iron, which can be only vivianite. The presence of the bones in the ferruginous water explains its formation, the bones affording the phosphoric acid from the phosphate of lime.

This fact recalls to mind an observation made some years since by Schlossberger, who detected in the stomach of an ostrich that had died suddenly two nails surrounded with an unctuous material of a bluish colour, which colouring matter the author found to consist of a phosphate of iron, having the composition of vivianite.

The bones mentioned above were in a perfect state of preservation, and afforded a skeleton of gelatine when treated with hydrochloric acid, proving that gelatine does not resist the absorption of the ferruginous compound. We know nothing as to their exact age. The presence of gelatine is not a matter of surprise, as is shown by the discovery of it in the fossil horn of an Aurochs (*Bos urus*) by Braconnot*, and the antediluvian soup of Cuvier. They probably date back hardly two centuries. Whatever the time, they illustrate the interesting fact of the modern origin of vivianite and the conditions favouring it.—Silliman's *Journal* for May 1856.

On the supposed Existence of Iodine, and Detection of Nitric Acid, in the Air. By M. KLETZINSKY.

The author contradicts the opinions of Chatin and Grange, the former of whom has been led by his investigations to the conclusion that the absence of iodine in the air, water, and food are the principal causes of goitre and cretinism, his examination of the air of Vienna, a district free from goitre and cretinism, proving that it contained no iodine. He also asserts that nitric acid is always present in the air in summer.

As the author found that none of the carbonates of soda and potash, caustic potash, soda, or lime, occurring in commerce, were perfectly free from iodine, he prepared a solution of caustic potash perfectly free both from iodine and nitric acid, and of a tolerably high degree of concentration, with which he filled a Liebig's bulb-apparatus, which was united by means of caoutchouc at one end to a common aspirator, and at the other to a glass conducting tube, which fed the apparatus with free air filtered through cotton-wool. After the operation had been carried on for four months (July to October), sulphuret of ammonium was added to the contents of the potash-tube, which were then evaporated to dryness and exhausted with alcohol. Neither the alcoholic extract nor the residue contained any trace of iodine. The saline residue contained no trace of iodine, but gave the most unmistakeable reactions of nitric acid.—Heller's *Archiv*, vols. x. to xii. p. 384.

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* Journal de Physique, August 1806.

Note on the Preparation and Properties of Arsenic Acid.

By E. Kopp.

The following process has been found the most advantageous in the preparation of large quantities of arsenic acid. Upon 400 kilogrms. of arsenious acid in powder, 300 kilogrms. of nitric acid of spec. grav. 1·35 are poured very slowly. The operation is carried on in a cistern of the capacity of 1500 litres; the reaction commences almost immediately, the temperature rises more and more, and a very brisk ebullition takes place, accompanied by a very great disengagement of nitrous vapours. To prevent these from losing themselves in the air, where their abundance would exercise a very injurious action upon the surrounding vegetation, the strong draught of a very high chimney is employed to make the reddish vapours, in conjunction with atmospheric air and the vapour of water, pass through several condensing worm-tubes. These worm-tubes are formed of very large stone-ware pipes filled with well-cleaned coke, which is constantly moistened by a slender stream of water or weak nitric acid, the produce of a previous condensation. In this way a nitric acid of spec. grav. 1·15 to 1·18 was produced, representing from two-thirds to three-fourths of the acid employed. In from twenty-four to thirty-six hours, the liquid arsenic acid, which was perfectly limpid and of the consistence of concentrated sulphuric acid, was drawn off from the cistern by a leaden siphon. Care having been taken to keep the arsenious acid in excess during the reaction, the arsenic acid contained a small quantity of it in solution, but the addition of $\frac{1}{1000}$ to $\frac{1}{1500}$ of concentrated nitric acid to the liquid whilst still warm was sufficient to effect complete oxidation.

The liquid arsenic acid thus obtained, if left to itself for some time when the external temperature does not exceed 59° F., often sets into a semi-fluid mass in consequence of the formation of limpid and transparent crystals; this is the case especially when it is agitated. The crystals are sometimes in the form of elongated prisms, sometimes in that of rhomboidal laminæ. They are extremely deliquescent, dissolve almost instantaneously in water, producing a considerable degree of cold (the temperature is lowered about 59° F.), and contain 24 per cent. of water. They are therefore As^2O^5+4Aq. This is tribasic arsenic acid with 1 atom of water of crystallization. I have several times obtained magnificent crystallizations, presenting a deceptive resemblance to a fine crystallization of sulphate of soda. The crystals liquefy when heated to 212° F., the water is evolved, and a whitish deposit, which becomes more abundant when the liquid is allowed to cool, is formed. This deposit, which has the appearance of thick cream, is composed of a multitude of little needles, which, when strongly pressed between leaves of bibulous paper, contain about 19 per cent. of water, and are As^2O^5+3Aq. This hydrate is very easily obtained, even on the small scale, by evaporating any solution of arsenic acid for a long time on the water-bath. It dissolves readily in water, but without producing noticeable changes of temperature.

This acid may serve to furnish As^2O^5+4Aq, the preparation of which on the small scale presents some difficulty. For this purpose, a solution of arsenic acid is evaporated on the water-bath until its density is about 2·2. On cooling, As^2O^5+3Aq is deposited abundantly in the form of a white cream, above which are limpid mother-liquors of an almost oily consistence. Equal parts of the mother-liquor and of the white deposit are then taken; the latter is dissolved in a little less than half its volume of water, and the solution is poured into the mother-liquor. In a short time an abundant crystallization of As^2O^5+4Aq is formed.

If, instead of evaporating a solution of arsenic acid at 212° F., the temperature is raised to 284° or 356° F., crystals of a new form (they appear to be rectangular prisms) make their appearance; they are hard and brilliant, adhere strongly to each other, and only contain 13·5 per cent. of water, forming the acid As^2O^5+2Aq. The mother-liquor of these crystals has the spec. grav. 2·365 at 61° F. At 212° F. its density is not more than 2·227. It is therefore one of the most dense of aqueous solutions.

Bihydrated arsenic acid also dissolves pretty readily in water, and produces a strong elevation of temperature when tolerably large quantities are operated with. If a very concentrated solution of this acid be kept for some time at 392° F., and then raised slowly to 402°·8 F., the transformation of the bihydrated into the monohydrated acid will be observed at a particular moment. The liquid, which evolves very little aqueous vapour, becomes suddenly turbid, then pasty, and is finally converted into a nacreous mass of dazzling whiteness. At the same time, after a very short period of projection, craters are formed, through which aqueous vapour is disengaged with considerable force and with a hissing noise.

The nacreous mass, removed as soon as it appears dry from the action of heat, contains about 7·3 per cent. of water, and constitutes monohydrated arsenic acid, As^2O^5+Aq. This acid, which is rather difficult to obtain free from anhydrous acid, dissolves but slowly in cold water; in contact with warm water, the solution still takes place with ease and with a great evolution of heat. In all these solutions the arsenic acid passes into the state of ordinary trihydrated acid.

The different acids, heated nearly to a dull red heat, furnish anhydrous arsenic acid. This is no longer an acid, but an inert body, without action upon litmus, and insoluble in water, ammonia, &c. It may remain for days exposed to moist air without becoming damp; nevertheless in course of time it liquefies, and reproduces the ordinary trihydrated acid. When heated to redness it is decomposed, without fusion, into arsenious acid and oxygen; the latter escapes. To fuse it, a considerable quantity must be very rapidly submitted to a cherry-red heat. The greater part is decomposed and volatilized, but the remainder forms a yellowish-white ingot. The presence of a small quantity of alkali greatly facilitates the fusion.

Before placing the preparation and use of arsenic acid in the hands of workmen, I thought it my duty to try its action upon the organism. The following is a summary of my observations:—Hydrated arsenic acid, applied to the skin, soon produces blisters exactly similar to burns; the ulcers proceeding from these healed without the least difficulty. When the hands are frequently left in contact with a solution of arsenic acid, sufficiently diluted not to act as a caustic, nothing is felt for a considerable time. By degrees a painful sensation is experienced, principally under the nails, which at last becomes positively and strongly painful; finally, a considerable swelling takes place, the fingers double their bulk, the swelling extends gradually to the whole hand, and even to the arm, and at the same time febrile symptoms are manifested. By care, and especially by frequently washing the hands in lime-water, these symptoms rapidly disappear.

I have ascertained the presence of arsenic in the excretions, both liquid and solid. In other respects I found no alteration in general health, only that in the two months during which I was almost daily operating with arsenic acid, I observed an increase in the weight of the body of 10 kilogrms. When I left off occupying myself with this acid, my body returned in nine or ten weeks to its ordinary weight of 75 kilogrms.

M. Kopp's note was accompanied by a specimen of cotton-stuff printed in red, in which the white patterns were removed by means of arsenic acid. It is in seeking to substitute arsenic acid for tartaric acid for this purpose, that he was led to the researches of which some of the results are given in this note. He remarks that secondary as this application is in importance, it has nevertheless caused the consumption of several thousand kilogrammes of arsenic acid annually.—*Comptes Rendus*, June 2, 1856, p. 1060.

On the Behaviour of Iodide of Silver towards Ammonia.
By Dr. A. Vogel, Jun.

The yellow precipitate furnished by iodide of potassium with nitrate of silver, is not dissolved by ammonia, but acquires a paler colour therein. The author has found that this change of colour is owing to a combination of the iodide of silver with ammonia.—Buchner's *Neues Repert.* vol. v. p. 53.

On Protosulphate of Nickel. By C. Marignac.

According to Marignac, the protosulphate of nickel in quadratic crystals, to which the same amount of water has hitherto been ascribed as to the rhombic salt $\mathrm{NiO, SO^3+7HO}$, only contains 6 equivs. of water. From a solution of pure protosulphate of nickel he obtained, at 59° to 68° F., the rhombic crystals, isomorphous with sulphate of zinc and sulphate of magnesia; at 86° to 104° F. quadratic, and at 122° to 158° F. monoclinometric crystals. These crystals showed the following composition:—

	Rhombic crystals.		
	Calculated.	Found.	
NiO	26·71	..	26·38
$\mathrm{SO^3}$	28·46	..	28·47
$\mathrm{7HO}$	44·83	44·62	45·15

	Quadratic crystals.		
	Calculated.	Found.	
NiO	28·53	28·32	
$\mathrm{SO^3}$	30·41	30·42	
$\mathrm{6HO}$	41·06	41·26	41·59

	Monoclinometric crystals.				
		Found.			
	Calculated.				
NiO	28·53	27·79			
$\mathrm{SO^3}$	30·41	29·82			
$\mathrm{6HO}$	41·06	42·39	41·55	41·58	41·08

Marignac remarks that even Mitscherlich* found 30·14 and 29·88 per cent. of sulphuric acid in the quadratic salt. When the rhombic crystals are converted by exposure to the light of the sun into aggregations of quadratic crystals, a loss of water takes place, which Marignac determines at 6·87 per cent.; the conversion of $\mathrm{NiO, SO^3+7HO}$ into $\mathrm{NiO, SO^3+6HO}$ requires a loss of weight of 6·40 per cent. The monoclinometric crystals remain transparent above 104° F.; at ordinary temperatures they gradually become opake without loss of weight, and are probably converted into aggregations of quadratic crystals.

Dimorphism was therefore ascertained to occur in $\mathrm{NiO, SO^3+6HO}$, but not in $\mathrm{NiO, SO^3+7HO}$.

From solutions of sulphate of magnesia at about 158° F., of sulphate of zinc at 122° to 131° F., and of protosulphate of cobalt at 104° to 122° F., the author obtained crystals of the composition $\mathrm{RO, SO^3+6HO}$, isomorphous with the monoclinometric protosulphate of nickel, $\mathrm{NiO, SO^3+6HO}$.—Liebig's *Annalen*, xcvii. p. 294, March 1856.

ANALYTICAL CHEMISTRY.

Testing of various Organic Substances by Chromate of Potash and Sulphuric Acid. By M. Eboli.

According to M. Eboli, Professor of Chemistry and Mineralogy at the Academy of Medicine in Lima, the behaviour of organic substances towards chromic acid and sulphuric acid may be employed for their detection. The process may be employed in chemical jurisprudence.

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* Poggendorff's Annalen, xii. p. 146.

It is as follows:—1 to 2 milligrms. of the substance to be tested are put into a watch-glass, and 5 to 6 drops of sulphuric acid diluted with its weight of water are let fall upon it. A small fragment of chromate of potash is then laid in the fluid, and the colorations produced are carefully observed. Each change of colour lasts for some hours.

Morphia.—Nickel-green; then copper-green; lastly, dark dingy green.

Sulphate of Morphia.—Nickel-green; then copper-green; finally, dark yellow.

Acetate of Morphia.—Nickel-green; then copper-green; lastly, bluish-green.

Quinine.—Scheele's green; then a fine yellowish-green; lastly, dark green.

Sulphate of Quinine.—Nickel-green; then copper-green; lastly, dingy yellow.

Ferrocyanate of Quinine.—Dingy green; afterwards leaf-green; then dingy yellow; and finally, chocolate colour.

Cinchonine.—Scheele's green; then a fine yellowish-green; finally, a dark dingy yellow.

Sulphate of Cinchonine.—Scheele's green; then copper-green; and lastly, dark dingy yellow.

Veratrine.—Dingy green; then bottle-green; then nickel-green and turbid, becoming clear subsequently; afterwards copper-green and turbid; and lastly, dark dingy yellow.

Atropine.—The first tint, nickel-green, only appears in the course of a few minutes; it then passes to yellowish-green; and lastly, becomes dingy greenish-yellow, letting fall a yellowish precipitate, which is soluble in alcohol.

Delphinine.—Dingy green; then clear, and afterwards turbid nickel-green; finally, dingy yellowish.

Lupuline.—After some time greenish-yellow and turbid; finally, dingy greenish-yellow.

Codeine.—Scheele's green; then nickel-green; afterwards copper-green; and finally, dark dingy green.

Daturine.—Copper-green; lastly, greenish-blue.

Strychnine.—Very intense violet, almost black at the points of contact; then yellowish-violet; lastly, in two days, blue. The violet reaction has already been observed by Graham and Hofmann, but the subsequent changes of colour have not hitherto been noticed.

Caffeine.—No reaction.

Naphthaline.—No reaction.

Piperine.—Yellowish-green; then nickel-green; lastly, dingy green.

Cantharidine.—With this, concentrated sulphuric acid must be employed, and it must be heated nearly to boiling over the spirit-lamp. The flame is then removed, and the chromate of potash put in, when a brisk effervescence takes place, and a splendid green mass is produced, which dissolves in the course of a few hours, and finally becomes of a turbid leaf-green colour.

The author intends submitting another series of organic bodies to the same test. He remarks, in conclusion, that it will not do to substitute a solution of chromate of potash for the crystallized salt. With a solution the reaction takes place so instantaneously, that it is impossible to follow the changes of colour.—*Messagero de Lima, Archiv der Pharm.*, cxxxv. p. 186.

New Method of determining Iron in the Urine by means of Permanganate of Potash. By Dr. Böcker.

The protoxide of iron is converted into peroxide by permanganate of potash, but the latter is thus deprived of colour. About 100 cub. centims. are evaporated to dryness in a platinum dish, reduced to ashes by means of a little nitric acid, and dissolved in pure muriatic acid. Half a drachm of pure zinc is added, and it is gently heated on the sand-bath, when a sufficient quantity of muriatic acid to dissolve all the zinc is added. The fluid is then filtered, and a normal solution of permanganate of potash is added to the filtrate from a graduated burette until the fluid acquires a fine rose colour. The amount of permanganate of potash used is then read off, and from this the quantity of iron in the urine is calculated.

The zinc however must previously be tested as to its amount of iron in the following manner:—Half a drachm of zinc is dissolved in muriatic acid, filtered, and diluted with water; it is then tested with the normal solution, and the amount used with it is deducted from the entire quantity employed with the urine. In this way Böcker found 0·001 grm. of iron in 100 cub. centims. of normal urine, whilst $\frac{1}{2}$ drm. of his zinc contained 0·0022 grm. of iron.—*Prager Vierteljahrschrift*, iii. p. 131.

Determination of Butter in Milk. By M. Marchand.

Marchand's lactobutyrometer consists of a straight glass tube as the vessel of reception, which terminates in a narrower glass tube closed on one side. Up to $\frac{18}{20}$ths of its contents it is divided into 3 equal parts, of which that nearest the opening again has its three upper tenths divided into 100 parts, 10 of which are carried on beneath the line of demarcation.

For use, the first division is filled with milk, to every 10 cub. centims. of which a drop of caustic soda is added; this is covered with the same volume of æther, the two fluids are thoroughly mixed together, and the last division is then filled with alcohol of spec. grav. 0·864 to 0·833°, and the whole well shaken together. The instrument is then immersed in a water-bath of 109°·4 F., and left there in a vertical position until the temperature of the water-bath has fallen to 86° F. The volume of fat which has separated on the surface is determined by reading off the degrees which it occupies from above downwards to the lowest level of the meniscus. The corresponding weight of butter for each kilogramme is found in a table.—*Journ. de Chim. Méd.*, Nov. 1855, p. 641.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Compounds of Carbon and Iron, and their Influence on the Production of Pig Iron. By A. GURLT.

[Concluded from page 236.]

AFTER these remarks it will be as well to consider the somewhat modified theory of the production of cast iron, and to follow a charge from the furnace-mouth to the crucible. The charge gradually descending as the furnace becomes heated, arrives at the zone of reduction with a temperature of about 400° C. (750° F.). Here the oxides of iron, manganese, sulphur, and phosphorus are gradually reduced, the electro-negative substances combining the moment they are set free with the electro-positive to form metallic sulphides and phosphurets. After the reduction of all the oxides is effected, which is completed about the junction of the belly with the boshes, the charge, now consisting of metal, phosphurets, and sulphurets, with the materials of the slag, enters the zone of carburation, and comes in contact with a large excess of carbonizing gases, viz. oxide of carbon and cyanogen. By its intimate contact with these carbonizing gases and the carbon of the fuel at the high temperature here existing, the reguline metal existing in the state of soft malleable iron uncombined with any electro-negative body becomes carbonized, that is to say, it unites chemically with carbon, which it abstracts from the carbonic oxide and cyanogen gases proportionately as it sinks deeper in the boshes. In most blast-furnaces, however, the boshes are considerably contracted at the base, so that the charge is detained, relatively speaking, sufficiently long in this region to combine with its maximum of carbon, passing into the condition of tetracarburet. In the normal working of the furnace then there is always one portion of the iron saturated with carbon when it enters the zone of fusion. In the zone of fusion the pig iron and the earthy matters are melted, and sink together through the hottest part of the furnace, the zone of oxidation, into the crucible, where it collects. If now the temperature existing in the zones of fusion and oxidation were not much higher than the point of fusion of the specular iron, the tetracarburet found in the zone of carburation would arrive undecomposed, and solidify after tapping as white cast iron with little or no graphite. If the charge remained long enough in the zone of carburation to saturate the whole of the iron with carbon, specular iron would be produced. In either case, however, the whole of the carbon exists chemically combined with the iron, with the occasional exception of that small quantity of graphite separated by silicium which is not visible on the fracture. The reduction of the silicium seems to commence about the melting-point of specular iron as it exists in very small quantity in this kind of iron, and in white cast iron produced from easily fusible ores at a low temperature; in gray cast iron, however, which is known to require a much higher temperature and more refractory ores, it exists in much larger quantity. The very considerable difference of temperature which must prevail in the furnace during the preparation of white and gray cast iron, may be judged of from the fact, that with the same ores and fuel the quantity of carbon required to produce gray cast iron will be 50 per cent. greater than is necessary for white cast iron. When, therefore, the temperature of the zones of fusion and oxidation considerably exceeds the melting-point of specular iron, which must always be the case in the preparation of gray cast iron, the tetracarburet formed will be decomposed into octocarburet and carbon, separating in the form of graphite. The melted crude iron arrives in the crucible as octocarburet, and solidifies, after casting, into gray cast iron. By incomplete decomposition of the tetracarburet, mottled cast iron is produced, consisting of a mixture of tetracarburet and octocarburet similar to white cast iron, but distinguishable from this by the particles of graphite disseminated through it.

In order to ascertain how far the views expressed above as to the influence exerted by the carburets of iron on the production of pig iron would agree with the results of analysis, the author calculated a series of the most trustworthy analyses of pig iron by Karsten, Berthier, Bodemann, Bromeis, and others. In this calculation, the fundamental principle was adhered to, that all the electro-negative constituents of the cast iron were chemically combined with the electro-positive according to those known compounds in which the maximum of the latter is contained as $(FeMn)^4 P$, $(FeMn)^8 S$, and $(FeMn)^8 Si$. The only exception being in the case of the specular iron, where, for the sake of analogy with the carburets, a tetrasiliciuret has been assumed.

The following are the results of the calculation:—

I. *White Cast Iron.*

Specular Iron from Spathose Iron-Ore from Saynerhütte. Karsten.

Carbon	5·112	$Fe^4 C$	Fe	94·188	99·300
Sulphur......	0·001		C	5·112	
Iron	94·887	$Fe^8 S$	Fe	0·014	0·015
Copper	trace		S	0·001	
	100·000			99·315	

Specular Iron from Lohhütte. Karsten.

Carbon......	5·411	$Fe^4 C$	Fe	88·099	97·291
Silicium	0·366		Mn	4·245	
Sulphur Phosphorus	traces		C	4·947	
Iron.........	90·797	$Fe^4 Si$	Fe	1·698	2·064
Manganese ..	4·245		Si	0·366	
Copper	0·179				
	99·998			99·355	

Specular Iron from Spathose and Brown Iron Ores, Hammhütte.

Karsten.

Carbon	5·140	$(Fe, Mn)^4 C$	Fe	89·726	95·606
Sulphur	0·002		Mn	0·794	
Phosphorus	0·080		C	5·086	
Silicium	0·560	$Mn^4 Si$	Mn	3·130	3·686
Iron	89·720		Si	0·556	
Manganese	4·300	$Mn^4 P$	Mn	0·556	0·636
			P	0·080	
		$Mn^8 S$	Mn	0·028	0·030
			S	0·002	
	100·002			99·958	

White Cast Iron, Calder Iron Works, England. Berthier.

Carbon	1·90	$Fe^4 C + Fe^8 C$	Fe	53·750	55·671
Graphite	0·50		C	1·921	
Sulphur	1·40	$Fe^8 Si$	Fe	12·108	13·308
Phosphorus	1·20		Si	1·200	
Silicium	1·20	$Fe^8 S$	Fe	19·474	20·874
Iron	93·42		S	1·400	
Manganese	0·38	$Fe^4 P$	Fe	8·088	9·288
			P	1·200	
		Graphite			0·500
	100·00				99·641

White Cast Iron, Hammhütte. Berthier.

Carbon	2·910	$Fe^4 C + 3Fe^8 C$	Fe	95·202	98·112
Sulphur	0·010		C	2·910	
Phosphorus	0·080	$Mn^8 Si$	Mn	0·109	0·110
Silicium	0·001		Si	0·001	
Iron	95·202	$Mn^8 S$	Mn	0·140	0·150
Manganese	0·890		S	0·010	
		$Mn^4 P$	Mn	0·528	0·608
			P	0·080	
	99·093			98·980	

White Cast Iron from Spathose Iron Ore, Mägdesprung. Bromeis.

Carbon	2·52	$Fe^4 C + 6Fe^8 C$	Fe	88·532	91·052
Graphite	0·50		C	2·520	
Sulphur	trace	$Fe^8 Si$	Fe	3·329	3·659
Phosphorus	0·40		Si	0·330	
Silicium	0·33	$Mn^4 P$	Mn	3·270	3·670
Iron	92·06		P	0·400	
Manganese	3·27	Graphite Copper			0·610
Copper	0·11				
	99·19				98·991

II. *Gray Cast Iron.*

Mottled Cast Iron from Sphærosiderite, Firmy. Berthier.

Carbon	1·00	$2Fe^4C+Fe^8C$	Fe	24·84	25·84
Graphite	0·18		C	1·00	
Sulphur	3·75	Fe^8Si	Fe	13·11	14·41
Phosphorus ..	0·38		Si	1·30	
Silicium	1·30	Fe^8S	Fe	52·36	56·11
Iron	93·39		S	3·75	
		Fe^4P	Fe	2·56	2·94
			P	0·38	
		Graphite............			0·18
	100·00				99·48

Mottled Cast Iron from Königshütte, Hartz. Bodemann.

Carbon	2·78	Fe^4C+Fe^8C	Fe	77·562	80·342
Graphite	1·99		C	2·780	
Phosphorus ..	1·23	Fe^8Si	Fe	7·164	7·874
Sulphur	trace		Si	0·710	
Silicium	0·71	Fe^4P	Fe	0·290	9·520
Iron	93·29		P	1·230	
		Graphite			1·990
	100·00				99·726

Mottled Cast Iron, South Staffordshire. Wrightson.

Carbon......	2·72	Fe^4C+Fe^8C	Fe	91·310	94·030
Graphite	0·26		C	2·720	
Phosphorus ..	0·37	Fe^8Si	Fe	1·109	1·219
Sulphur......	trace		Si	0·110	
Silicium	0·11	Fe^4P	Fe	2·493	2·863
Iron	95·80		P	0·370	
		Graphite			0·260
Manganese Calcium Sodium	0·74	Mn Ca Na	....		0·740
	100·00				99·112

Gray Pig Iron, Königshütte, Hartz. Bodemann.

Carbon	1·44	Fe^8C	Fe	53·726	55·166
Graphite	2·71		C	1·440	
Sulphur	trace	Fe^8Si	Fe	32·388	35·598
Phosphorus....	1·22		Si	3·210	
Silicium	3·21	Fe^4P	Fe	8·223	9·443
Iron..........	92·42		P	1·220	
		Graphite............			2·710
	101·00				102·917

Gray Cast Iron from Spathose and Brown Iron Ores, Hammhütte.
Karsten.

Carbon......	2·08	$(Fe, Mn)^3 C$	Fe		
Graphite	2·37		Mn	78·70	80·78
Silicium	1·31		C	2·08	
Phosphorus ..	0·08	$Fe^8 Si$	Fe	13·14	14·45
Iron	86·73		Si	1·31	
Manganese ..	7·42	$Fe^4 P$	Fe	0·75	0·83
			P	0·08	
		Graphite			2·37
	99·99				98·43

Gray Iron from Lancashire Hæmatite. Miller.

Carbon	2·217	$Fe^8 C$	Fe	82·716	84·933
Graphite	0·538		C	2·217	
Silicium......	0·951	$Fe^8 Si$	Fe	9·595	10·546
Sulphur......	0·150		Si	0·951	
Phosphorus ..	trace	$Fe^8 S$	Fe	2·086	2·236
Iron	95·777		S	0·150	
		Graphite............			0·538
	99·633				98·253

A glance at the interpretation of the above analyses will be sufficient to show the close agreement between the results, assuming the hypothesis of the two subcarburets of iron, and to prove the probable correctness of the views on the theory of the production of pig iron above put forth.

Lastly, to exhibit analytically the influence which the different temperatures at which the respective varieties of cast iron are produced exert on their composition, the author undertook a series of analyses of such varieties of pig iron as were produced from the same ores, fluxes, and fuel, but at different degrees of temperature. These were five varieties from the celebrated iron-works of Gartsherrie in Scotland, made from black-band iron-stone with raw coal and limestone from the coal-measures. Their chemical composition was as follows:—

	1.	2.	3.	4.	5.
Carbon	1·347	1·021	1·793	1·925	2·451
Graphite....	3·156	2·641	1·110	1·051	0·877
Silicium	2·721	3·061	2·165	1·895	1·124
Sulphur	1·267	1·139	1·480	1·614	2·516
Phosphorus	0·842	0·928	1·171	1·811	0·913
Iron	88·983	90·236	89·314	91·368	89·863
Manganese..	2·401	0·834	1·596	0·571	2·715
	100·717	99·860	98·629	100·235	100·459

1. Very gray iron, with graphite in large flakes; spec. grav.=7·15.
2. Gray iron, with much graphite but in small flakes; spec. grav =7·21.
3. Mottled gray iron; spec. grav.=7·21.

4. Mottled gray iron; spec. grav.=7·25.

5. White cast iron, with radiate crystalline fracture; spec. grav. =7·41.

Of these pig irons 1 and 2 were produced at the highest temperature, that is to say, with the largest consumption of fuel, while in the three others it was diminished. The blast had a considerable pressure, and the air was heated above the melting-point of lead for the production of the gray pig.

The above analyses plainly show, that with the diminution of the temperature the amount of the graphite and silicium also diminishes, and, on the other hand, that the chemically-combined carbon and the sulphur steadily increase, while the amount of phosphorus varies; for the amount of manganese also no law can be discovered. The large amount of sulphur in these Scotch irons is, no doubt, chiefly owing to a considerable quantity of pyrites often disseminated through the coal used as fuel.

The theoretical calculation of the five analyses agrees with the above assumption, that the two varieties 1 and 2 are composed of $Fe^8 C$, and the three others of mixtures of $Fe^8 C$ and $Fe^4 C$, furnishing a new proof of the correctness of the above views on the influence exerted by the carburets of iron on the chemical composition of pig iron.

On the Analysis of Cast Iron.—As the analysis of cast iron is often accompanied with considerable difficulty, and the various methods proposed afford results differing widely from each other, the author gives the following methods made use of by himself, after many comparative trials had convinced him of their advantage and accuracy.

Determination of the Carbon, Graphite, and Silicium.—The substance is placed in a glass flask with about four times its weight of chloride of silver recently precipitated and well washed, a saturated solution of muriate of ammonia poured over it, and allowed to stand ten to twelve days at a moderate temperature. The iron is hereby converted into protochloride and dissolved, but is again decomposed into sesquioxide and sesquichloride by absorption of oxygen. The silicium is oxidized, and the carbon and graphite remain undissolved. When the iron is completely dissolved, the solution is gently boiled with a few drops of hydrochloric acid to redissolve any portions of sesquioxide which may have separated, the contents of the flask are then brought on a filter, and the residue washed first with water, and afterwards with cyanide of potassium, to dissolve any undecomposed chloride of silver; this must be continued until the filtered fluid no longer exhibits the reactions of silver; the washing is then completed with pure water, and the filter dried and weighed; the weight of the silver, graphite, carbon, and silica is thus obtained; a certain portion of this residue is then boiled for some time with a solution of caustic soda; the silica and chemically-combined carbon are dissolved and separated from the silver and graphite, which are weighed, and the difference will give the weight of the former substances.

The solution of soda is evaporated to dryness after being acidulated with hydrochloric acid, redissolved and filtered; the carbon and silica remain on the filter, which is burnt; the weight of the silica is thus obtained, that of the carbon being determined by the difference.

To determine the graphite, it is only necessary to dissolve the silver in dilute nitric acid; the graphite remains unaltered, and may be weighed.

Determination of the Sulphur.—It is not advisable to determine the sulphur in cast iron by precipitating the sulphuric acid by a salt of baryta from a solution in aqua regia, as it is difficult to avoid a portion of nitrate of baryta accompanying the precipitate, which cannot afterwards be separated by washing. It is better to dissolve about 1 grm. of the iron in dilute sulphuric acid with the assistance of heat, passing the hydrosulphuric acid gas into a moderately dilute solution of acetate of lead. The sulphuret of lead thereby produced is collected on a filter, well washed, converted into sulphate of lead by means of nitric acid, and weighed.

Determination of Iron, Manganese, and Phosphorus.—From a solution of the iron in aqua regia, in which these substances will exist as chloride of iron, protochloride of manganese, and phosphoric acid, the iron is precipitated by the addition of pure dry carbonate of soda in the cold, accompanied by the phosphoric acid as phosphate of iron, while the manganese remains in solution as carbonate of protoxide of manganese dissolved by the excess of carbonic acid. The precipitate is collected without loss of time, and thoroughly washed with cold water; it is ignited and weighed, and gives the amount of iron and phosphoric acid. A weighed portion of this precipitate is fused with four times its weight of a mixture of $3NaO\,CO^2 + 2KO\,CO^2$, for twenty to thirty minutes, in a platinum crucible, whereby the phosphoric acid is brought into combination with soda; the fused mass is treated with water and filtered, the solution saturated with pure nitric acid, and boiled some time to expel the whole of the carbonic acid; a few drops of acetic acid and solution of acetate of lead are then added, whereupon phosphate of lead is precipitated, which is washed and ignited; it contains in 100 parts, 8·523 of phosphorus. The manganese is easily obtained from the solution in carbonic acid by the addition of caustic soda or potash; the precipitate, which is white, but gradually becomes brown, is collected, ignited, and weighed as deutoxide.

Determination of Zinc.—In some specimens of cast iron minute quantities of zinc are found, which can only be estimated by a separate experiment. From a solution in aqua regia the iron is precipitated by succinate of soda, afterwards the zinc by carbonate of soda; the manganese remains in solution; the carbonate of zinc is ignited and weighed as oxide of zinc.

Determination of Arsenic and Copper.—Arsenic and copper are precipitated by hydrosulphuric acid from the solution of the iron in aqua regia, separated from each other by sulphide of ammonium, and determined in the usual manner.—*Polytechn. Centralbl.*, 1856, p. 366–379.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Chinoline and its Homologues. By C. GREVILLE WILLIAMS, Assistant to Dr. Anderson, University of Glasgow.

TWENTY-TWO years have now elapsed since Runge first published his remarkable experiments on coal-naphtha*, and it would perhaps be difficult to instance any chemical investigation which has formed the point of departure of a greater number of researches. When we consider the vast quantity of bodies which have, first and last, been obtained from coal-tar, it might appear that little more remained to be done—that the mine was exhausted; but so far from this being the case, the discovery of one substance has only served to pave the way for the isolation of others.

Among the bodies examined by Runge, there was one which apparently possessed comparatively few features of interest; indeed its very name was intended to express its supposed inability to produce coloured reactions, a feature which, in the chemistry of the time, militated greatly against its claims to notice. I have used the expression "supposed inability," because I shall show further on, that this substance is capable, under certain conditions, of affording extremely brilliant colorations. Eventually, Gerhardt†, by acting on quinine, cinchonine, and strychnine with hydrate of potash, obtained the same body. The first chemist who succeeded in procuring any of its compounds in a state of tolerable purity was Hofmann, whose analysis of the platinum-salt is very nearly exact. But, at the time of that analysis, he was of opinion that the products obtained from coal and chinoline were essentially different, an opinion which he subsequently retracted. In the meantime, the alkaloid, as obtained from cinchonine, was examined by Bromeis‡ and Laurent§, their results however not elucidating the composition of the basic fluid obtained in the manner alluded to.

Some time since, I undertook the examination of the bases produced by destructive distillation of the bituminous shale of Dorsetshire, and found them to be identical with those from bone-oil*. I now began to see the great probability that all processes of destructive distillation of nitrogenous matter at very elevated temperatures would result in the formation of the same classes of alkaloids, and subsequent researches have only tended to confirm this view. In a little paper, "On some of the basic constituents of Coal-naphtha, and on Chrysène†," I have given a table, showing the extraordinary similarity of the basic products derived by dry distillation from Dippel's oil, coal, the Dorset shale, and cinchonine. The last of these researches was undertaken in the endeavour to throw light upon the discrepancies in the results of the chemists who had previously examined chinoline, the experiments being embodied in a paper which appeared in the Transactions of the Society last year. In that communication‡ I showed that the fluid usually known as chinoline, and supposed to have the formula $C^{18} H^7 N$, had, in fact, a very complex constitution, and contained, in addition to that base, six others. As my chief object at that time was to demonstrate the real nature of the decomposition which cinchonine undergoes at an elevated temperature in the presence of alkalies, I did not make a minute examination of the chinoline itself, as I conceived it to be sufficient for the purposes of that investigation to show that a base of the formula $C^{18} H^7 N$ did really exist in the fluid. This fact was by no means a matter of course, for the analyses of the chinoline from cinchonine previously published were so conflicting, that it was a difficult matter to derive a formula from them. Hofmann's analyses were made upon a product from coal-tar, and the formula he gave as the expression of his results was $C^{18} H^8 N$. But as an even number of atoms of hydrogen in a body containing an equivalent of nitrogen was incompatible with views now almost universally received of the constitution of organic bodies, $C^{18} H^7 N$ was taken by most chemists as the true formula of the base from coal-tar. But the wide differences in the analyses of the chinoline obtained by distilling cinchonine with potash induced Gerhardt§ to express doubts as to whether $C^{18} H^7 N$ or $C^{20} H^9 N$ was the correct formula, although he appears to lean towards the latter, for he places it at the head of the section, but nevertheless shows that the formula is open to doubt by annexing a note of interrogation to it. I have shown the cause of the variable nature of the results obtained by other experimenters, and have proved the existence of a homologous series, of which, until I commenced this investigation, only one member was known.

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* Poggendorff's Annalen, xxxi. p. 65 and 513; and xxxii. p. 308 and 328.

† Revue Scientif., x. p. 186; Compt. Rend. des Trav. de Chim., 1845, p. 30.

‡ Liebig's Annalen, lii. p. 130; and Ann. der Chem. und Pharm., lii. p. 130.

§ Ann. de Chim. et de Phys., [3] xxx. p. 368.

Many circumstances conspire to render a detailed examination of chinoline a problem of interest, for perhaps no other body, known for an equal length of time, and investigated by so many hands, is so erroneously described in the manuals of organic chemistry. In fact, there are few things stated regarding it that are not more or less incorrect.

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* Quart. Journ. Chem. Soc. Lond., July 1854.

† Chem. Gaz., Nov. 1, 1855.

‡ Chem. Gaz. vol. xiii. pp. 301, 325.

§ Traité de Chimie Organique, troisième partie, p. 148.

Chinoline has however been invested with an artificial interest, from a supposed intimate connexion between it and quinine, and an equally supposititious parallelism between the action of heat upon the last-named alkaloid, and upon the hydrated oxide of tetramethylammonium, while the real points of attraction which it possesses have been neglected, or supposed not to exist.

The first incorrect idea of the connexion between chinoline and quinine may be very briefly disposed of. It was founded upon the supposition that chinoline was the sole product of the action of hydrate of potash, at a high temperature, upon quinine. In this manner it was easy to construct an equation by which it was made to appear that quinine, *minus* a certain number of equivalents of carbon, hydrogen, and oxygen, yielded chinoline.

Another supposed connexion between the two alkaloids was a very beautiful one, and one that, at the time when $C^{18}H^{8}N$ was the received formula for chinoline, could scarcely have failed to suggest itself to the eminent chemist, whose particular train of research led him to examine the action of iodide of methyle upon the natural and artificial alkaloids. It is well known that iodide of tetræthylammonium, by treatment with oxide of silver, yields hydrated oxide of that base, which is rendered obvious by a glance at the following equation:—

$$N\left\{\begin{matrix}C^{4}H^{5}\\C^{4}H^{5}\\C^{4}H^{5}\\C^{4}H^{5}\end{matrix}\right\}I+AgO+HO=N\left\{\begin{matrix}C^{4}H^{5}\\C^{4}H^{5}\\C^{4}H^{5}\\C^{4}H^{5}\end{matrix}\right\}O,HO+AgI;$$

and if we follow out the same equation, substituting iodide of methylchinoline-ammonium* for iodide of tetræthylammonium, we find that at first sight

$$\underbrace{C^{20}H^{11}N,I}_{\substack{\text{Iodide of methyl-}\\\text{chinoline-ammonium.}}}+AgO+HO=\underbrace{C^{20}H^{12}NO^{2}}_{\text{Quinine.}}+AgI$$

appears a reaction likely to take place†; unfortunately, however, there are two reasons why it is impossible, the first being that iodide of methyl-chinoline-ammonium is represented by $C^{20}H^{10}N,I$, instead of $C^{20}H^{11}N,I$; and the other, that the action of oxide of silver upon the methyle and æthyle compounds of the nitryle bases of this class is more complex than would be supposed from the first equation, and the known success of the reaction with the iodides of the ammonium bases derived from the alcohol radicals alone.

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* Supposing for the moment the old formula for chinoline ($C^{18}H^{8}N$) to be correct.

† I have vainly searched through the Chemical Journals for any paper by Dr. Hofmann, tending to show the real nature of the action of oxide of silver upon iodide of methylchinoline.

So much has been said about the artificial formation of quinine from the leukole of coal-tar, that I have appended a few reasons for concluding that it is impossible by any analogous process to that previously described. Quinine, according to Strecker's experiments*, takes up only 1 equiv. of the alcohol radicals, and is therefore concluded with safety to be a nitryle base. Chinoline affords still more complete evidence of belonging to the same class, for not only is it incapable of taking up more than 1 equiv., but by the operation it becomes converted into a fixed alkaloid. Now any process for making artificial quinine by means of the reactions mentioned above would result in the formation of an ammonium base, which must of necessity have a totally different constitution to quinine. It may be worth while, for a moment, to glance at the formidable difficulties by which the artificial formation of such a base as quinine is surrounded. In the first place, in the present state of our information, it appears to consist of three radicals, united and having 1 equiv. of nitrogen and 2 of oxygen attached. Now, to acquire a knowledge of the constitution of these three radicals (one of which, in all probability, is oxidized) is a problem involving a new mode of research, the key to which appears for the present to be hidden. And even supposing the three radicals known, they have to be formed; and then to combine them with the addition of an equivalent of nitrogen, without destroying the group, presents a task of no ordinary difficulty.

I should not have entered upon this branch of the subject had it not been for the manner in which the possibility of the formation of quinine, by the method above alluded to, has been accepted as a reality, which is the more remarkable from the manner in which Hofmann cautioned chemists against placing too much reliance upon the success of the process.

As it is my wish to correct, as far as my information will permit me, the erroneous views which have been formed of the relations between chinoline and quinine, I return to the supposed similarity between the action of heat upon quinine and the hydrated oxide of tetramethylammonium. This part of the subject is the more interesting, as it appears to have formed one of the links in the chain of reasoning, which led to a belief in the possibility of converting leukole into quinine by the successive actions of iodide of methyle and oxide of silver. As the fixed base, hydrated oxide of tetramethylammonium, by heating yields trimethylamine, the difference being $C^2 H^4 O^2$, so quinine less $C^2 H^4 O^2$ yields the old formula of leukole†, thus,—

$$\underbrace{C^8 H^{13} NO^2}_{\substack{\text{Hydrated oxide of}\\ \text{tetramethylammonium.}}} - C^2 H^4 O^2 = \underbrace{C^6 H^9 N.}_{\substack{\text{Trimethyl-}\\ \text{amine.}}}$$

$$\underbrace{C^{20} H^{12} NO^2}_{\text{Quinine.}} - C^2 H^4 O^2 = \underbrace{C^{18} H^8 N.}_{\text{Leukole.}}$$

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* Researches in Organic Chemistry, by Adolph Strecker; Comptes Rendus, xxxi. 49.

† Quart. Journ. Chem. Soc., vol. iv. p. 328.

The identity in kind of the above equations presupposes two conditions, neither of which exist, the first being the correctness of the old formula for chinoline (or leukole); the second, its being the sole basic product in the distillate from the cinchona alkaloids.

The next prevalent error with regard to chinoline is that its salts have less tendency to crystallize than the generality of nitryle bases, whereas, in fact, the reverse (with some exceptions) is the truth. I have seldom seen salts more easy to crystallize than the nitrate, oxalate, and bichromate of chinoline, while its double salts, with platinum, gold, palladium, uranium, and cadmium, are beautiful substances; the same may be said of the iodides of the methyle, æthyle, and amyle compounds. The erroneous idea alluded to arose from previous experimenters working on an impure substance.

The only means for determining the constitution of chinoline up to the present time has been Dr. Hofmann's analysis of the platinum-salt from a base extracted from coal-tar, for the combustions of the base itself yet made are very unsatisfactory. Annexed are the results hitherto obtained*:—

	Hofmann.			Bromeis.		$C^{18}H^7N$.	$C^{20}H^9N$.
C	82·67	82·88	82·34	82·74	82·78	83·70	83·91
H	6·56	6·25	6·10	6·11	5·88	5·41	6·29
N	11·28	..	..	..	..	10·89	9·80

A glance at the above numbers shows that no conclusion can be drawn from them; and when it is considered that chinoline and lepidine only differ by 0·21 in their per-centage of carbon, it becomes evident that careful analyses of the salts of these bases are the only means by which their history and composition can be rendered certain. The platinum-salt of chinoline possesses characters which render it peculiarly well adapted for this purpose, inasmuch as it differs totally from the corresponding compound from the Dippel and aniline series in its great insolubility. I therefore selected this compound as a means of ascertaining the purity of the various fractions obtained in the course of the investigation, and which were intended for conversion into the various salts described further on. Sometimes I was contented with merely a platinum determination; at others, I ascertained by combustion with chromate of lead, the per-centage of carbon and hydrogen, and in this manner the analyses quoted below were obtained. In my former paper I gave the result of three combustions of the platinum-salt of chinoline, and three platinum determinations; the salts analysed were obtained from fractions boiling at a somewhat lower temperature than those the details of the analyses of which are given below. The following analyses were made with salts obtained from fractions boiling about 460°, which is probably very nearly the boiling-point of chinoline:—

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* Gerhardt, Traité, troisième partie, p. 149.

	I.	II.	III.	Mean.
Carbon	32·36	..	..	32·36
Hydrogen	2·74	..	..	2·74
Nitrogen	..	..	..	..
Chlorine	..	..	..	..
Platinum	29·30	29·26	29·30	29·29

In the following table, the result of all my analyses (including those in my former paper) is compared with the numbers required by theory, the analysis just quoted being the fourth in the series:—

	I.	II.	III.	IV.	V.	VI.	Mean.	Theory.
C	31·93	32·24	32·52	32·36	..	..	32·26	32·19
H	3·09	2·62	2·58	2·74	..	..	2·76	2·39
N	..	..	..	..	..	..	..	4·17
Cl	..	..	..	..	..	..	..	31·74
Pl	29·44	29·30	29·60	29·30	29·40	29·26	29·38	29·51

It will be seen that there is a slight excess both in the carbon and hydrogen of these analyses. This arises from the presence of a small quantity of lepidine, the platinum-salt of the two bases being too nearly of the same degree of solubility to allow of separation by fractional crystallization. This source of error is much lessened in the other salts, their formation, in most cases, being a process of purification. Platinochloride of chinoline is very sparingly soluble in cold water, requiring 893 parts for solution at 60° F.

It is to be remembered that all the chinoline compounds mentioned in this paper were made from a base procured by distillation of cinchonine with potash, the coal-chinoline requiring a tedious series of purifications, in addition to the fractional distillations, before it could be obtained pure enough for conversion into compounds fit for analysis. The platinum-salt is however more easily obtained in a pure state from the coal bases than most other compounds of this alkaloid.

In the following table, the mean result of my analyses of the platinum-salt of chinoline is compared with those obtained by other observers*, whose numbers have been recalculated according to the present atomic weight of carbon:—

	Hofmann.		Gerhardt.			Bromeis.			Grev. Williams.	
									Mean.	Calc.
C	32·06	..	32·99	32·46	32·51	33·31	33·42	33·33	32·26	32·19
H	2·58	..	3·14	3·14	3·28	2·71	2·83	2·68	2·76	2·39
N	..	..	4·42	..	..	3·98	4·21	4·00	..	4·17
Cl	30·96	..	..	..	..	..	..	..	..	31·74
Pl	29·27	29·11	27·80	28·08	27·69	28·23	28·34	28·81	29·38	29·51

Only the first of these analyses was made from a base extracted from coal-tar; all the others were obtained from chinoline, produced by destructive distillation of cinchonine with potash.

Laurent, by mixing hot alcoholic solutions of hydrochlorate of chinoline and bichloride of platinum, obtained after twenty-four hours fine yellow needles; but, on examinatian under the lens, it was found not to be a homogeneous crystallization, for a small quantity of little grains had also deposited*. I have not found that any observer, except myself, has subjected the bases produced from cinchonine to a systematic fractionation before forming the platinum-salt. The fraction analysed by me had been rectified fourteen times, and was nearly constant between 460° and 470°.

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* Gerhardt, *loc. cit.*

Aurochloride of Chinoline.—The only account of this beautiful salt I have been able to find is in Dr. Hofmann's paper on the bases of coal-tar, where he merely states that it corresponds in colour and other properties with the gold-salt of aniline; but the latter appears† to be a yellow precipitate which rapidly becomes brown in the air, and therefore differs considerably from the chinoline-salt, which is quite permanent under the same circumstances. As obtained by me from a specimen of chinoline of considerable purity, it was in the form of slender canary-yellow needles, sparingly soluble in cold water, and precipitating instantly on the addition of a solution of terchloride of gold to a moderately strong solution of hydrochlorate of chinoline. 3·883 grs. of aurochloride of chinoline, dried at 212°, gave on ignition 1·625 gr. of gold=41·85 per cent.; the formula $C^{18} H^7 N, HCl + AuCl^3$ requires 42·00.

Palladiochloride of Chinoline.—Dr. Hofmann describes this salt in his paper, previously quoted, as resembling that from aniline, but M. Müller‡ states the latter to be *yellow*; I found, however, that when moderately concentrated solutions of chloride of palladium and hydrochlorate of chinoline are mixed, a copious deposit of *chestnut-brown* crystals takes place. This salt is moderately soluble in water. It requires a very strong heat to give pure metallic palladium.

3·423 grs. of palladiochloride of chinoline gave, on powerful ignition in a porcelain capsule, 0·725 gr. of palladium=21·18 per cent.; the formula $C^{18} H^7 N, HCl + PdCl$ requires 20·96.

Cadmium-Salt Chinoline.—The experiments of Croft, and more especially Von Hauer, have shown that cadmium forms well-defined crystalline salts with the chlorides of the alkalies, alkaline earths, and the chloride of ammonium. Before I became acquainted with the results of the latter chemist, I had been engaged in a series of experiments, made with a view of extending our knowledge of the double salts formed by the hydrochlorates of the alkaloids with metallic chlorides. The information at present in our possession on this subject is very limited. The only salts of the class alluded to which have been analysed are those formed with platinum, gold, palladium, and mercury. Now the salts of the latter metal vary greatly in constitution, and are moreover somewhat troublesome to analyse. I have therefore made a few experiments, with a view to ascertain what other metals than those mentioned above yield chlorides capable of combining with the alkaloids to form well-crystallized double salts. In the present communication, however, I only notice those formed by the chlorides of cadmium and uranyle with chinoline.

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* Gerhardt, *loc. cit.*, and Laurent, Ann. de Chim. et de Phys. [3], xxx. 368.

† Gerhardt, Traité, tome troisième, p. 86.

‡ Ann der Chem. und Pharm., lxxxvi. 368.

When moderately concentrated solutions of hydrochlorate of chinoline and chloride of cadmium are mixed, the fluid solidifies, with rise of temperature, to a snow-white mass of crystals. If the solutions are not too strong, they are obtained in the form of needles, occupying a great bulk when in the mother-liquor, but shrinking very much when pressed. They are less soluble in alcohol; I therefore used that fluid to wash them. The alcoholic washings, when kept for some time, deposit needles, often an inch long, but so silky and fragile as to be preserved of their original size with difficulty. They retain their colour perfectly, and, with the exception of losing 2 equivs. of water of crystallization, are quite unaltered by drying for a few hours at 212°. The salt volatilizes at a considerably higher temperature, without residue. The quantity at my disposal was very limited; and being therefore obliged to work on small quantities, I found it inconvenient to estimate the cadmium as oxide by the usual process, as the carbonate of cadmium, when precipitated from solutions containing chinoline at the boiling heat, not only has a strong tendency to pass through the filter, but adheres to the paper so strongly as to cause a loss of metal by reduction and volatilization during incineration. The precipitate was too light to be collected by decantation. I obtained, however, an accurate result by precipitating with sulphuretted hydrogen, and collecting the sulphide of cadmium on a weighed filter:—

	I.	II.	III.	IV.	Mean.			
C	30·94	30·89	..	..	30·92	18	=108	30·99
H	2·48	2·58	..	..	2·53	8	8	2·29
N	..	..	4·02	..	4·02	1	14	4·02
Cl	..	..	..	..	..	3	106·5	30·56
Cd	..	..	..	32·07	32·07	2	112	32·14

It is evident therefore that the formula for the salt, dried at 212°, is $C^{18}H^{7}N, HCl+2CdCl$.

Several examples of salts of the same constitution occur in inorganic chemistry, some of which have been examined by M. von Hauer, who terms them chlorobicadmiates. The chinoline salt, if merely dried by exposure to the air, contains 2 equivs. of water, for at 212° it loses 5·41 per cent.; theory requires 4·91. The excess arises from a little moisture adhering somewhat tenaciously to the crystals.

Hydrochlorate of Chinoline and Chloride of Uranyle.—If double carbonate of uranium and ammonia, dissolved in hydrochloric acid, is added to a strong solution of hydrochlorate of chinoline, the fluid rapidly becomes filled with short, brilliant, yellow needles, and in a few minutes the whole fluid solidifies, so that the vessel may be inverted without the contents escaping. From more dilute solutions, prismatic crystals are deposited, sometimes of considerable size. The salt is of a rich yellow colour, and is very soluble in water. It was quite free from any trace of ammonia. The mother-liquid was removed by washing with alcohol. The quantity at my disposal was too small to allow of a complete examination of all its properties.

The salt, dried at 212°, furnished on analysis C 31·87, H 2·77, Cl 20·97; the formula $C^{18} H^7 N, HCl+(Ur^2 O^2) Cl$, which requires C 32·05, H 2·37, Cl 21·07, appears therefore to be the correct expression of the analysis, and it agrees in constitution with the anhydrous ammoniochloride of uranyle of Peligot. It is my intention to examine the double compounds of uranium with other organic bases.

Binoxalate of Chinoline.—The great discrepancy in the results of Runge and Hofmann with regard to the oxalate of chinoline made me desirous of ascertaining the nature of this salt. According to the former chemist, leukole (chinoline) has such a great tendency to form a crystalline oxalate, that this property is its marked characteristic; Hofmann, on the other hand, could only obtain it in the form of a confused, radiated, glutinous mass, deposited when the solution had reached a certain state of concentration. I found, however, that if 24·3 parts of chinoline are added to 16·5 parts dry oxalic acid, dissolved in a small quantity of water, the whole solidifies to a white crystalline mass of the consistence of soft cheese. The salt cannot be obtained pure by a random admixture of the ingredients, as, although the chief tendency appears to be to form the binoxalate, yet other compounds are also formed in sufficient quantity to prevent constant analytical results from being obtained, unless the above proportions are used. The salt, before being employed for analysis, must be recrystallized from alcohol once or twice, when it forms fine silky needles. It is partially decomposed by exposure for two days to 212°, with evolution of chinoline, a salt being formed intermediate in composition between the binoxalate and quadroxalate. It is necessary therefore to dry it for analysis *in vacuo* over sulphuric acid.

Experiment gave C 60·07, H 4·44; the formula $C^{22} H^9 NO^8$ requires C 60·27, H 4·11.

Nitrate of Chinoline.—In some respects my experiments on this salt tally with those of Dr. Hofmann, in others they differ considerably. It was obtained by the last-named chemist by allowing a mixture of leukole and dilute nitric acid to rest under a bell-jar; after some time the salt crystallized in confused concentric needles, which were obtained white and dry by pressure between folds of filtering-paper. He does not appear to have analysed it. I found that if, after an excess of nitric acid slightly diluted was added to chinoline, the fluid was evaporated on the water-bath, a pasty mass was obtained, which solidified on cooling. From a hot alcoholic solution fine white needles soon deposited, which were infusible at 212°, and unalterable in the air. Dr. Hofmann, on the contrary, found his salt to fuse on moderate heating, and to become rapidly blood-red by exposure to the air; these are evidently the characters of an impure substance. The nitrate of chinoline was burnt with oxide of copper, a long column of copper turnings being placed in the front of the tube.

Experiment gave C 55·94, H 4·27; the formula $C^{18}H^{8}N^{2}O^{6}$ requires C 56·25, H 4·17.

Chinoline gives a very marked reaction with strong fuming nitric acid, and which also shows its great stability. If a few drops of the base are allowed to trickle down the side of a test-tube, and a small excess of the acid is added, the two combine with violence, the portion of alkaloid adhering to the sides is converted by the fumes of the acid into long needles, and when cold the whole fluid solidifies to a beautifully white crystalline mass of pure nitrate. No nitrochinoline, or any other decomposition product, is formed if the base be free from impurities.

Bichromate of Chinoline.—Gerhardt, in describing this salt*, merely states, that chromic acid in solution gives, with pure chinoline, an orange-yellow crystalline precipitate, and that the dry acid decomposes the base with inflammation; Dr. Hofmann, in his paper on the coal bases, previously referred to, states that a short time after he had commenced the investigation of leukole, he was inclined to consider it the same as that Gerhardt obtained by the action of hydrate of potash on quinine, cinchonine, and strychnine. He says however that he soon convinced himself that they were totally distinct, their behaviour towards a solution of chromic acid being quite dissimilar, for while chinoline and its salts gave a beautiful orange-yellow crystalline precipitate, leukole was oxidized and converted into a black resinous oil. Subsequently† Liebig announced, upon the authority of experiments made by Hofmann, that perfectly pure leukole gave the same crystalline precipitate with chromic acid. I have not been so successful as M. Hofmann; for although the chinoline and lepidine procured by destructive distillation from cinchonine have, in my hands, given salts of extreme beauty and purity with chromic acid, I have failed to obtain the same result with either the chinoline or lepidine from coal-tar. I have also boiled the bases from the latter source with dilute chromic acid to destroy impurities, and then separated them by distillation with potash, but they merely gave an oily precipitate with chromic acid. When dissolved in hydrochloric acid, and bichromate of potash is added, the same result occurs. I even took a platinum-salt of coal-lepidine, which yielded on combustion 34·48 per cent. of carbon and 2·97 hydrogen; and, after having reobtained the base by distillation with potash, endeavoured to procure from it a crystalline chromate, but in vain, a red oil being the only product. It is true, that when I added dilute chromic acid to chinoline from coal-tar, the sides of the tube acquired a coating of very minute brilliant points, which reflected light with a peculiar satin-like lustre; but the lens resolved them into oily globules. The following experiments were therefore made upon chinoline from cinchonine. Neither Gerhardt nor Hofmann have analysed the salt.

The beauty of the bichromate of lepidine, described in my last paper*, induced me to ascertain the composition and properties of the homologue next below it, in the anticipation that its outward appearance would be equally striking. But there are some slight differences in the two bodies; bichromate of chinoline is still less soluble than the other salt, and this prevents the crystals from being readily procured of so large a size. When dry it is much more violently decomposed by heat than the lepidine compound. The fixed product is however the same, namely, green oxide of chromium and carbonaceous matter. If the dry salt be placed in a capsule, and heat be very gradually applied, no change at first takes place, but suddenly it takes fire with explosive violence, and the greater part of the green oxide and carbon is projected. I prepared the salt for analysis by adding dilute chromic acid in excess to pure chinoline; at first the product is somewhat resinous, but immediately it is touched with a glass rod it becomes gritty and crystalline. The solid is then filtered off, the mass slightly washed, dissolved in boiling water, filtered to remove traces of an oily impurity, and on cooling the fluid becomes filled with brilliant yellow needles arranged in groups. It may be dried at 212° with safety, provided adhering moisture has been removed as much as possible by pressure between folds of filtering-paper. If the salt is previously moistened with hydrochloric acid, it may be ignited without explosion, and the green oxide estimated with accuracy. The combustion was made with oxide of copper:—

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* Traité de Chimie Organique, troisième partie, p. 150.

† Chem. Gaz., vol. iii. p. 251 (1845).

	I.	II.	III.				
Carbon	45·08	..	..	18	=	108	45·11
Hydrogen ..	3·49	..	..	8		8	3·34
Nitrogen	..	..	..	1		14	5·85
Chromium ..	..	22·40	22·28	2		53·4	22·31
Oxygen	..	..	..	7		56·0	23·39

Density of the Vapour of Chinoline.—In Dr. Hofmann's paper on the coal-bases, he states that a determination of the density of the vapour of leukole (chinoline) failed, owing to its leaving a yellow residue on distillation. I have not found this circumstance to operate sufficiently in the case of chinoline from cinchonine, to cause more error than is usually found in determining the vapour densities of bodies obtained by fractional distillation, and having so high a boiling-point. The specimen used, boiled in the fourteenth rectification between 460° and 470° F.:—

Temperature of air	13° C.
Temperature of vapour	277° C.
Pressure	751 millims.
Capacity of balloon	330 cub. centims.
Residual air	17·5 cub. centims.
Excess of weight of balloon......	0·4980 grms.

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* Chem. Gaz., vol. xiii. p. 301.

The formula $C^{18}H^{7}N$ requires

18 vols. carbon vapour ..	0·829	. 18 = 14·922
14 vols. hydrogen	0·0692	. 14 = 0·9688
2 vols. nitrogen........	0·9713	. 2 = 1·9426

$$\frac{17{\cdot}8334}{4} = 4{\cdot}4583$$

Experiment.	Theory. $C^{18}H^{7}N = 4$ vols.
4·5190	4·4583

[To be continued.]

On the Nature of the Torbane-hill Mineral, and its Products of Distillation. By A. Genther.

The author has investigated the nature of the mineral from Torbane Hill, near Bathgate in Scotland, which has already given rise to several disputes as to whether it is a true coal or a bituminous substance.

When ignited, this mineral burns quietly for some time with a luminous smoky flame; it does not melt, and its form remains unchanged. It contains a small quantity of hygroscopic water, losing only 0·5 per cent. in weight when dried. When boiled with solution of potash, it only yields alumina; muriatic acid extracts alumina and peroxide of iron. Alcohol and æther, when boiled with the mineral, remain colourless, and only take up a very small quantity of a yellowish-white semifluid body. The mineral contains 75·7 per cent. of carbon, 5·8 per cent. of hydrogen, and 0·3 per cent. of nitrogen.

In the dry distillation, only hygroscopic water passes over at 752° to 932° F.; at a higher temperature, a rather volatile colourless oil passes; at a temperature near a slight red heat, the distillate is a heavy brown oil; and when complete redness is attained, a yellow vapour passes, and condenses in the receiver to a dark brown, slightly fluid oil, which subsequently deposits a crystallizable substance.

The oily distillate has a neutral, the watery one a slightly ammoniacal reaction. In the whole, 100 parts of the mineral furnished 43·2 of fluid distillate, 42·0 of residue, and 14·8 of gas. The gas contained 57 to 74 per cent. of constituents condensable by chlorine.

The author first distilled the fluid oil with water, by which it was decomposed into a portion volatilizable with aqueous vapour and a residue. The first contains a very volatile oil, which passes even at 95° to 104° F., but the boiling-point of which constantly rises. The author endeavoured to separate this oil by fractional distillation, and it appeared from his analyses that all the fluid oils consisted of different but isomeric hydrocarbons of the formula $C^{n}H^{n}$. Their behaviour with chlorine and sulphuric acid also indicates this, as they combine with the former to form chlorinated oils, and are absorbed by the latter. The boiling-points of the different portions at the same time showed that several such oils were intermixed.

The distillate also contained paraffine and small quantities of picoline and phenole.

The first distillate, rectified with water, was separated by the author into two portions, one boiling below and the other above 284° F.

The oil remaining after distillation with water began to boil at 464° F., and the boiling-point then rose to 526° F. The two fluids could then be divided into fractions, with boiling-points lying between these limits.

The ashes of the mineral consisted of silica, 48·5; alumina, 39·1; and oxide of iron, 12·4.

Thus, both from its ashes and its products of distillation, this mineral is not a coal, for the true coals furnish much benzole, naphthaline, and phenole. The mineral, on the contrary, gave only a small quantity of phenole, and no benzole or naphthaline, but other substances polymeric with common coal gas. Genther therefore regards the Torbane-hill mineral as a bituminous shale. Microscopic examination showed no traces of vegetable cells.—Liebig's *Annalen*, xcvii. p. 277.

On the Monohydrochlorate of Turpentine, or Artificial Camphor.
By Dr. ALEX. BUTLEROW.

As it is yet far from being decided in what state the chlorine exists in the hydrochlorates of turpentine, the author made some experiments with several reagents upon the monohydrochlorate, so as to obtain products of double decomposition. The hydrochlorate was prepared from a turpentine which is known in Kasan as French turpentine, by passing dry chlorine gas into the distilled oil cooled to 32° F.; and the artificial camphor obtained was purified by pressure, washing with solution of soda, and recrystallization from alcohol.

The artificial camphor is not easily altered, but the double decomposition takes place at a high temperature under strong pressure, especially when the whole quantity of the two bodies is in solution at this temperature. Experiments showed, however, that the camphor may be decomposed without the agency of other bodies when in solution in aqueous alcohol; and this circumstance is very injurious to the completeness and preciseness of the decompositions.

After some experiments with various substances which did not give a complete decomposition, the author selected sulphocyanide of potassium. When the two bodies, with a quantity of alcohol sufficient for their solution, are heated two or three times to 302°–320° F. in a sealed tube, chloride of potassium separates, and the fluid contains no more camphor. When mixed with water, an oil separates, possessing a peculiar, strong, disagreeable, garlic-like odour, indicative of the presence of sulphur. This oil, when washed with weak solution of potash and distilled, contained sulphur and nitrogen, and the author expects to find in it a product of substitution containing sulphocyanogen. The same oil appears to be formed by the action of sulphocyanide of silver on artificial camphor.

The decomposition of the camphor with weak spirit takes place at 275° F., when the aqueous alcohol is present in sufficient quantity for its complete solution. Absolute alcohol, even when employed in great quantity and heated to 338° F., does not effect a complete decomposition.

When heated two or three times to 302°-320° F. with alcohol of spec. grav. 0·912, the whole of the hydrochlorate undergoes alteration; the fluid is acid, and contains hydrochloric acid, and when mixed with water, an oil which is lighter than water separates. At the same time some gas bubbles are evolved, which burn with a greenish flame. These are probably vapours of chloræthyle. The distilled product is colourless, possesses a remarkable odour of camphor, and appears to contain no chlorine.

When the monohydrochlorate is heated to 338° F. with distilled water, a little hydrochloric acid separates, but the greater part of the camphor remains unaltered.—*Chemisches Central-blatt*, June 14, 1856, p. 406.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Treatment of rich Argentiferous Minerals at Joachimsthal in Bohemia. By Adolph Patera, Professor at the Imperial School of Mines, Pzibram.

Some years ago I made experiments on the best method of treating the rich argentiferous minerals then recently found at Joachimsthal. My primary object was to remove the whole of the silver which they contained, and with this view I employed the method of "*extraction.*" I afterwards endeavoured to extract the cobalt and nickel at the same time as the silver. My researches, which have been pursued without interruption, have convinced me that the method employed presents incontestable advantages for the extraction of the silver, as well as the cobalt and nickel contained in the ores of Joachimsthal.

It is known from the researches of Karsten, that a portion of the silver contained in the ores roasted with chloride of sodium, to be afterwards subjected to amalgamation, passes to the state of chloride of silver. Afterwards, Gmelin and Rivero proposed the employment of ammonia, instead of mercury, to extract the chloride of silver; this method however has never been employed, unless it may be in France. At the commencement of the present century Wetzlar discovered that chloride of silver was soluble in a warm solution of common salt; and M. Augustin, of Mansfeld mines, has since availed himself of this property for the extraction of silver on the large scale.

As the chloride of sodium is not added at first to the ores to be prepared for amalgamation by roasting, it being the object to first convert the sulphurets into sulphates, M. Ziervogel abstained altogether from the use of chloride of sodium, confining himself to dissolving out the sulphate of silver produced by the roasting, and precipitating the metal by means of copper plates.

Neither of these methods was applicable to the minerals recently discovered at Joachimsthal, containing 5 marcs of silver in the centner (2½ per cent.), besides 5 to 10 per cent. of cobalt and nickel. The method of M. Augustin was defective, on account of the considerable loss of silver which takes place during the roasting with chloride of sodium. And the method of M. Ziervogel was inapplicable, as these minerals contained a large proportion of arsenic, and produced on roasting, arseniate of silver, insoluble in a solution of chloride of sodium.

The method of Gmelin and Rivero not having as yet been submitted to decisive practical proof, could not be applied to the ores of Joachimsthal.

I commenced my experiments by treating the antimonial silver, which is the richest mineral, with a solution of sulphuret of sodium, my intention being to dissolve the sulphuret of arsenic, and to precipitate the silver in the state of pulverulent sulphuret; then to convert the sulphuret of silver into chloride by means of chloride of copper; and lastly, to extract the chloride of silver by a solution of hyposulphite of soda or chloride of sodium.

This process, although theoretically correct, was found to be too complicated to be executed on a large scale; it had the further disadvantage of not admitting of the simultaneous extraction of the cobalt and nickel. I undertook therefore a series of experiments with the object of extracting these three metals at once; and my first attempts having been accompanied with success, I found myself in a position to submit to the Minister of Finance the details of a plan for proceeding on the large scale, much less expensive than the metallurgical treatment actually in use.

This process includes the following operations:—

1. Roasting.
2. Solution.
3. Precipitation of the silver.
4. Reduction of the silver.
5. Fusion of the silver.
6. Separation of the cobalt and nickel from arsenic and iron.
7. Separation of the nickel from the cobalt.
8. Precipitation of the nickel.
9. Reduction of the nickel.

1. *Roasting.*—The ore, reduced to about the size of a pea, is roasted in a small reverberatory furnace, while a current of steam is passed over it, as recommended by Regnault and Cumenge. Each furnace contains ½ cwt. They are formed like those commonly in use in Hungary, having a double sole for previously heating the ore, and chambers of condensation. The steam is delivered on to the ore, heated to redness, by means of three tuyères.

The roasting is conducted at a very moderate heat, the ore being stirred very seldom. Five or six hours after firing, the disengagement of vapours ceases, and the operation may be considered as complete at the end of six hours.

The roasted mass contains the silver in the metallic state, and the cobalt and nickel as yellow anhydrous arseniates. The dust deposited in the chambers is always small in quantity; it contains only the arsenic in the metallic state, minute fragments of the ore, and the ashes of the wood used in heating the furnace. The portion of silver existing in this dust is small relative to the richness of the mineral.

The roasting, when conducted in the manner described above, involves no loss of silver, as the chemical decomposition takes place at a very moderate heat, and the greater part of the substances volatilized is condensed by their contact with the vapour of water.

At first the ores were not reduced beyond the dimensions of a pea. In this state they were completely roasted, but their solution was accompanied with difficulty, and the residues contained an appreciable quantity of silver: I found it necessary to grind them after having moistened them, which was easily effected, the ore having become tender by roasting. Afterwards this became unnecessary, as the ores were reduced to a sufficient state of division.

2. *Solution.*—The solution was conducted in wooden vessels on portions of the calcined mineral weighing 37½ lbs., corresponding to ½ cwt. unroasted ore, employing weak sulphuric acid at a temperature of 40° C., obtained by means of steam. The residue was sufficiently washed after contact with the acid for five hours.

The employment of the sulphuric acid has for its object the extraction of the nickel and cobalt, and to prepare the silver insoluble in dilute sulphuric acid for the subsequent action of the nitric acid. The solution of sulphates of nickel and cobalt is decanted, and the ore is submitted to the action of *dilute nitric acid* at the same temperature, 40° C. The nitric acid acts energetically on the silver, with evolution of intensely red vapours. This disengagement of red vapours ceases after four or five hours, although the solution is still strongly acid, a proof that the acid contains all that it is capable of dissolving at 40° C.; the residue is then washed with hot water until the washings no longer contain a trace of silver or nickel. When the acid has ceased to act at a temperature of 40° C., if the temperature be raised to ebullition the red vapours are again disengaged, proving that the acid acts upon a further portion of silver and nickel, and the silver contained in the residues is reduced to $\frac{11}{300}$, while the residues obtained at a temperature of 40° C. contained $\frac{15}{100}$ of the silver contained in the raw mineral. These trials, often repeated, prove that in operating at a temperature superior to 40° C., it is possible to obtain an additional quantity of silver without increasing the proportion of acid. The wooden vessels in which I operated absorb a certain portion of the solution of silver. I analysed the ashes of two staves, forming part of a vessel composed of fourteen such staves. I found ¼ oz. of silver in them, which would render it probable that the whole vessel, including the bottom, had absorbed about 2 oz. of metallic silver. It would be easy to obtain this silver by burning the vessels and washing the ashes, which would leave a residue rich in silver to add to that under operation. It is moreover probable that in causing the nitric acid to act on the roasted ore at a higher temperature, the same quantity of silver would be obtained in less time and with a smaller consumption of acid.

3. *Precipitation of the Silver.*—The nitric acid, after having acted

on the mineral previously roasted and treated with sulphuric acid, contains silver, nickel, cobalt, a little iron and arsenic acid. The silver is precipitated in the form of chloride on the addition of chloride of sodium; this precipitation may be much facilitated by agitating the solution with a disc of wood pierced with holes and attached to a handle. The solution of nickel is decanted by means of a siphon from the precipitated chloride of silver, which is reduced to the metallic state. The decanted solution retains in suspension, however, fine particles both of the chloride of silver and the powdered mineral, which it deposits completely in about three hours. This deposit is reduced with the rest of the chloride, and the solution, which now only contains the nickel and cobalt, is submitted to an ulterior treatment for the extraction of these two metals.

4. *Reduction of the Chloride of Silver.*—The chloride of silver, after having been very carefully washed, is placed in a vessel with water acidulated with sulphuric acid, and reduced by fragments of iron. The metallic silver is washed, filtered through canvas, pressed, and dried. This washing should be conducted with care; otherwise, on fusing the silver, a ferruginous matte (*lech*) would be obtained, or a speiss containing arsenic, cobalt or nickel, according as the silver might be impregnated with the arseniate of cobalt or nickel, or the sulphate of iron. These salts would be reduced by the charcoal employed in the fusion, producing argentiferous products, which would hinder and complicate the operation.

5. *Fusion.*—The metallic silver thus obtained was fused in graphite crucibles, and formed into ingots; a small amount of flux being added, sufficient to scorify a small per-centage of calcined ore which still accompanied the silver. It is however easy to avoid this inconvenience by allowing the solution to stand and clarify a sufficient length of time.

6. *Separation of the Nickel and Cobalt from Arsenic.*—The solution from which the silver was precipitated as chloride, is submitted to a particular treatment for the separation of the nickel and cobalt. To separate the arsenic acid, I selected a method which is said to be also employed at Birmingham. Sesquichloride of iron, obtained by the action of hydrochloric acid on calcined sulphate of iron, is added to the solution in sufficient quantity to form a basic arseniate of iron, which is precipitated together with an excess of oxide of iron (if care is taken to add the sesquichloride in excess), when the solution is neutralized by carbonate of lime in fine powder. The protoxide of iron separates very slowly from the neutral solution; it may be accelerated however by boiling, and for this reason, and also to diminish the volume of the solution freed from the arsenic and iron, it was evaporated in leaden boilers.

7. *Separation of the Nickel from Cobalt.*—To the solution, after evaporation and completely free from arsenic and iron, hypochlorite of lime (chloride of lime) was added, which converts the protoxide of cobalt into peroxide, which is insoluble in the neutralized solution, and is therefore precipitated in the form of a black powder. The hypochlorite of lime should be employed with caution, as an excess would precipitate the nickel in company with the cobalt.

When the precipitate has completely deposited, the supernatant liquor is removed by means of a glass siphon, and the oxide of cobalt is brought on to a cloth filter. In almost all cases the oxide so prepared is sufficiently free from foreign matters to be offered as an article of commerce, and in any case it would be easy to free it from any small quantity of impurity which might accompany it. Frequent experiment has shown that it is better not to precipitate the whole of the cobalt by the hypochlorite of lime, but rather to leave a small portion with the nickel, a slight mixture of cobalt having no injurious effects on the quality of the nickel, while a very small quantity of the latter metal is sufficient to deteriorate considerably the quality of the oxide of cobalt.

8. *Precipitation of the Nickel.*—The solution, after the precipitation of the cobalt, is treated in large wooden tanks with milk of lime recently prepared. A hydrated oxide of nickel is thus obtained, which is brought on to cloth filters, and pressed and dried.

9. *Reduction of the Oxide of Nickel.*—The oxide of nickel, after being dried, is heated to redness and reduced to a fine powder; it is then made into a paste as stiff as possible by the addition of 5 per cent. of coarse flour with syrup of beet-root and sufficient water. This mass is compressed in a frame, and then cut into cubes, which are dried as rapidly as possible in order that the farina may not enter into fermentation, taking care not to char the cubes, as they would be rendered brittle. These cubes, after being dried and covered with powdered charcoal, are heated to whiteness for the reduction of the nickel. The metallic nickel, whose particles are agglutinated by incipient fusion, retains its cubical form, unless it contains foreign matters. In order to avoid this inconvenience, it may be calcined previous to its reduction with 10 to 15 per cent. of soda, which removes the last traces of sulphur and arsenic. The surface of these being rough, they may be polished by friction, by placing them in a barrel filled with water, and capable of revolving on its axis. Some of these cubes of nickel were exhibited at the Exposition Universelle at Paris.

The minerals on which I operated in the manner described above contained on the average 3 per cent. of silver, 2 per cent. of cobalt, and 8 per cent. of nickel. The total quantity treated was 41 quintals (or cwts.). The loss in silver amounted to $\frac{155}{1000}$; that of the nickel and cobalt was not ascertained, but I have every reason to believe that it was trifling. This new method is much less costly than that hitherto pursued. I do not think it applicable to the treatment of any but rich silver ores, although I have only tried it with those of Joachimsthal. Further experience may enable me to modify it so as to apply it with advantage to poor ores.

The method I have followed for the extraction of the silver has furnished it in a state of almost absolute purity, and also the cobalt. The nickel, with regard to its external form, is quite equal to that of Saxony.

An analysis has been made of the nickel of Joachimsthal, in the laboratory of the Imperial Institute of Geology, by M. Charles Hauer; it gave the following results:—

Nickel	86·40
Cobalt	12·00
Iron	0·22
Sulphur	0·10
Silica	1·40
Copper	trace
	100·12

In performing this analysis, the iron was separated by ammonia; then a current of chlorine was passed through the solution containing the cobalt and nickel in the state of chlorides. The cobalt was afterwards precipitated by carbonate of baryta.—*Annales des Mines*, série 5, tome viii.

The author quotes analyses to show that his nickel is purer than that made on the continent. This may be so; but 12 per cent. of cobalt is too much to leave with the nickel. The loss to a large firm would be considerable, as cobalt is more than twice the value of nickel.

In the works of Messrs. Evans and Askin of Birmingham the separation of these two metals is complete. A sample of their nickel, analysed by me some years ago, gave the following results:—

Nickel	97·920
Iron	0·210
Silicon	1·870
	100·000

with trace of carbon.

It was free from cobalt. T. H. Henry.

Improved Process for the Manufacture of Phosphorus.

By Hugo Fleck.

In the course of last year the author published a separate memoir, in which he described an improved process for the manufacture of phosphorus. By this process 100 lbs. of fresh bones furnish 6 to 7 lbs. of phosphorus, and 10 to 20 lbs. of gelatine, whilst the older process only gave 4 to 5 lbs. of phosphorus.

The bones, properly cleaned and broken up, and freed as much as possible from fat, are macerated with dilute muriatic acid, by which chloride of calcium and acid phosphate of lime ($CaO, 2HO, PO^5$) are produced. The maceration is continued until as much as possible of the earthy matter is extracted, and only the cartilage remains. The latter is watered, immersed in lime-water, again washed, and then employed in the production of bone-gelatine, which turns out very pure and clear.

The fluid containing the chloride of calcium and the acid phosphate of lime is evaporated. This operation is carried on in glazed stone-ware pans, as metal pans do not present sufficient resistance to the action of the acid fluid. The evaporating pans are heated by the flue from the phosphorus-furnace, and the evaporation is continued until the fluid marks about 38° B. It is then allowed to flow out of the pans and cool, when acid phosphate of lime separates in fine crystals. A further quantity of these is obtained by the evaporation and cooling of the mother-liquor. From the mother-liquor of the second crystallization the portion of phosphate still dissolved in it is obtained by mixing it with milk of lime, when phosphate of lime separates, which is treated with muriatic acid, like the residue from the retorts. The acid phosphate of lime, which cannot be washed on account of its solubility, is freed as far as possible from mother-liquor, either by pressing it between cloths, or by spreading it upon a porous plate and producing an imperfect vacuum beneath the latter, when the atmospheric pressure forces the mother-liquor through the plate, upon which the salt forms a white nacreous mass, which crackles between the fingers. This is warmed and mixed with one-fourth of powdered charcoal, passed through a sieve, and then put into the retorts.

For retorts, the author recommends clay cylinders, which, like the retorts of the gas-houses, are placed in fives over each fire. The tubes from each five retorts open into a common receiver; this is of the shape of a muffle, and is placed in a channel through which a stream of water is allowed to flow. The first receiver is connected with a second, similarly arranged. The fuel used is coke and coal. If the acid phosphate of lime was not well freed from the mother-liquor, which contains chloride of calcium, muriatic acid will be formed during the distillation, and thus a smaller amount of phosphorus will be obtained. The mixture of phosphate of lime and charcoal remaining in the retorts is reduced to ashes on iron plates, which are laid on the phosphorus-furnace and heated by its fire. The residue of phosphate of lime is then mixed with the phosphate formed by the addition of lime to the mother-liquor, and treated with muriatic acid. By this means chloride of calcium and acid phosphate of lime are again produced; the latter is separated and worked for phosphorus. In this way the entire amount of phosphorus in the bones, with the exception of unavoidable loss, is obtained.

The cartilage, isolated from the bones by means of muriatic acid as above described, is covered with water and exposed to a current of steam, until the solution forms a concentrated jelly, and this, when brought into form, dries on cooling into solid cakes. The phosphate of lime still in the membranes gives the gelatine a milky appearance, which is often increased by the addition of white lead, and the gelatine is then sold under the name of patent gelatine. The objections against the bone-gelatine obtained by extraction with acids, which have always prevailed amongst the tradespeople, arose from the employment of acids of too great strength. By the use of a muriatic acid of 7° B. at a moderate heat, and subsequent complete neutralization with lime-water (but not with milk of lime), we have not so much to fear a decomposition of the animal tissues, as that it would cause a diminution of the total product. A far greater injury is done by boiling the gelatine too long, and the treatment by steam is now justly recognized as a step in the manufacture of gelatine.—*Polytechn. Centralblatt*, 1856, p. 681.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Saponification of Fatty Bodies by the Anhydrous Oxides.

By J. Pelouze.

It is generally supposed that the saponification of fatty bodies can only take place in the presence of water. The author's experiments show that this opinion is not strictly correct, and that the anhydrous metallic oxides are as able to form soaps as the same bases when hydrated or mixed with water. He has principally employed suet, but has also operated upon oils, and his results may be regarded as applying to the different classes of neutral fatty bodies.

Anhydrous lime mixed with suet causes its complete saponification at about 482° F. The calcareous soap, decomposed by an acid, gives a quantity of fatty acid representing 95 to 96 per cent. of the weight of suet experimented on. The acids appeared identical in every respect with those obtained from suet by Chevreul.

The same soap with water yields glycerine mixed with a very small quantity of a calcareous salt, formed by an acid which is soluble in water, but the nature of which was not determined by the author.

During the reaction, the mixture of fat and anhydrous lime evolves a white smoke, with an odour of burnt sugar, in which that of acetone is also perceptible. These vapours, the weight of which does not generally exceed 2 to 3 per cent. of that of the suet, were condensed, and found to contain water, acetone, and glycerine. 10 parts of anhydrous lime are sufficient for the complete saponification of 100 of suet; with 12 or 14 parts the reaction takes place with much greater facility.

In operating with a considerable quantity of the mixture, it becomes difficult, even by removing the mass from the fire when the thermometer marks 482° to 500° F., to prevent the action from becoming violent. The mixture swells, and diffuses excessively thick vapours, the temperature rises rapidly, the decomposition acquires the characters of an ordinary destruction by fire, and the residue is a black carbonized mass.

Anhydrous baryta and strontia effect the saponification of suet and oils, like lime. Oxide of lead also produces the same decomposition very distinctly. By gradually raising the temperature of a mixture of massicot or litharge and suet, it is easy to produce a lead-soap, from which weak nitric acid extracts ordinary margaric, stearic, and oleic acids, amounting to 95 and 96 per cent. of the fat.

The author remarks, that these facts make no change in Chevreul's theory of saponification, but rather give it a new support. Chevreul, in showing that in the act of saponification the elements of water are fixed in the glycerine and fatty acids, has considered these acids not in their salts, but only in their state of liberty, after they had been eliminated from their soaps, an operation during which the acids combine with water. Thus when suet is saponified by oxide of calcium, if the anhydrous acids, which may be supposed ready formed in the fat, are entirely unaltered, this is not the case with the glycerine. The fat loses at least 2 per cent. of its weight, and this loss can only be attributed to a corresponding decomposition of the glycerine.

The anhydrous acids also saponify the neutral fatty bodies at a high temperature, but the action is slow, difficult, and incomplete. A current of dry muriatic acid gas was passed for several hours into suet kept at 482° F. Abundant vapours of Berthelot's chlorhydrine were produced. The residue yielded about half its weight of fatty acids to alkalies. A considerable portion of the fat was not saponified; it was mixed with colouring matters, which were not examined.

The author thought at first that the preceding observations might be applied advantageously to the manufacture of stearine candles, as the saponification of fat takes place much more rapidly with anhydrous lime than in the ordinary processes, requires less lime and less sulphuric acid for the decomposition of the soap; but he soon found that the use of slaked or monohydrated lime was likely to render more service to the arts. Slaked lime, mixed with fat in the proportion of 10 to 12 per cent., causes its complete saponification between 410° and 447° F. The glycerine remains intimately mixed with the calcareous soap. The latter is white, amorphous, semitransparent, and almost colourless; it yields glycerine to water. Weak muriatic and sulphuric acids separate the fatty acids, which still represent 96 per cent. of the fat employed. With 1 kilogrm. of fat and 120 grms. of monohydrated lime in powder, at a temperature of about 419° to 428° F., the saponification is completed in less than an hour; it only takes a few minutes if the temperature be rapidly raised to 482° F. With 15 per cent. of lime the operation is effected with still greater facility. This last soap is harder, whiter, and more easily pulverized than that made with less lime. The fatty acids separated from it are of great whiteness and purity. By the ordinary method, with a milk of lime at the temperature of ebullition of the mixture, the saponification of a similar quantity of fat requires at least twenty to thirty hours; and to effect it completely under these circumstances, a larger quantity of lime is necessary. In the manufactories, saponification by milk of lime usually lasts for a whole day.

The author formerly showed that the saponification of oils is effected in a few moments in an alcoholic solution of potash or soda. Now, he observes, the intervention of alcohol may be got rid of, and fat or an oil may be saponified in a few minutes by monohydrated lime, so that a complete saponification may be exhibited in a lecture-room, including not only the fatty acids, but also the glycerine produced by the operation.—*Comptes Rendus*, June 9, 1856, p. 1081.

Researches on Chinoline and its Homologues. By C. Greville Williams, Assistant to Dr. Anderson, University of Glasgow.

[Concluded from page 272.]

Action of Iodide of Methyle on Chinoline.

Hydriodate of Methyle-chinoline.—When an excess of iodide of methyle is added to chinoline, and the mixture, enclosed in a pressure tube, is heated for ten minutes to 212°, combination is perfectly effected, a finely crystallized hydriodate resulting. If this salt, which is perhaps more correctly called iodide of methyle-chinoline-ammonium, is treated in the cold with excess of oxide of silver, a strongly alkaline solution is obtained, containing the hydrated oxide of the ammonium base. The solution possesses little stability; on heating with potash, an excessively pungent odour is evolved, acting strongly on the eyes and mucous membrane of the nose. The solution reddens turmeric paper as powerfully as solution of caustic potash, and instantly restores the colour of reddened litmus. The reactions of this base generally are the same as those of the æthyle compound next to be described. The smell of a volatile base, a product of the decomposition of methyle-chinoline, is evolved from the moment of its formation; it appears to be methylamine.

By alternate precipitation of the hydriodate by nitrate of silver, hydrochloric acid, and bichloride of platinum, after removal of the chloride of silver, a sparingly soluble platinum-salt was obtained. The following is the result of its analysis:—

	I.	II.	III.	IV.	Mean.			
C	34·66	34·52	..	..	34·59	20=	120	34·33
H	3·11	3·00	..	..	3·06	10	10	2·86
N	..	..	..	..	..	1	14	4·01
Cl	..	..	..	..	..	3	106·5	30·47
Pl	..	..	28·20	28·19	28·20	1	99	28·33

Methyle-chinoline is therefore isomeric with lepidine, but has no other point of resemblance. The decompositions of the hydriodate almost exactly resemble those of the æthyle base; and as the atomic weight of the latter, being higher, gave it an advantage for experiment, I selected it for the purpose.

Action of Iodide of Æthyle on Chinoline.

Hydriodate of Æthyle-chinoline.—No action takes place on the mere addition of excess of iodide of æthyle to chinoline; but if the tube containing the mixture be sealed, and exposed for some hours to a temperature of 212°, the whole becomes a mass of crystals. When this is the case, and the tube cools, the end may be cut off, a tube bent twice at right angles attached by means of a cork, and, the pressure-tube being immersed in the water-bath, the excess of iodide of æthyle distilled over. The crystals are then dissolved out in a small quantity of hot alcohol, and the solution allowed to cool. The first crop is of a rich yellow colour, becoming of a pale lemon tint on recrystallization. In the state in which the salt is thus obtained, it possesses the property of becoming a deep blood-red at 212°, and regaining its normal tint on cooling; this peculiarity becomes much lessened by a repetition of the process. The crystals appear to be cubic, and are easily obtained of considerable size. They dissolve more readily in water than alcohol, but the latter is the best solvent for the purposes of crystallization.

Dried at 212°, they furnished on analysis C 46·53, H 4·41, I 44·12; theory requires C 46·32, H 4·21, I 44·56.

Platinum Salt of Æthyle-chinoline.—After adding nitrate of silver to a solution of hydriodate of æthyle-chinoline, as in making the iodine determination last mentioned, the excess of silver was removed by the addition of hydrochloric acid, the liquid filtered, and evaporated to a moderate bulk, on the addition of bichloride of platinum a rich golden-yellow precipitate of sparing solubility was obtained; it was first washed with a little water, and afterwards with alcohol.

6·813 grs. of platinochloride of æthyle-chinoline gave 1·847 gr. of platinum=27·11 per cent., agreeing with the formula $C^{22} H^{11} N, HCl + PtCl^2$, which requires 27·24.

It is evident that æthyle-chinoline is isomeric with cryptidine, the new base to be described further on.

Action of Oxide of Silver on Iodide of Æthyle-chinoline.

Hydrated Oxide of Æthyle-chinoline-ammonium.—A solution of iodide of æthyle-chinoline is decomposed with ease by oxide of silver, even in the cold, a colourless strongly alkaline fluid being formed, containing the fixed base corresponding to the hydrated oxide of tetræthylammonium. The solution instantly reddens turmeric paper, and restores the colour of reddened litmus. It precipitates solutions of sulphate of copper, sesquichloride of iron, acetate of lead, and corrosive sublimate. The addition of a small quantity to a red solution of bichromate of potash renders it yellow, by neutralizing the second equivalent of chromic acid. The solution of the base decomposes chloride of ammonium, liberating the ammonia freely.

The heat of a water-bath decomposes the solution of the hydrated oxide, with production of a splendid crimson colour, the sides of the basin where the liquid has dried becoming a brilliant emerald-green, passing in a few seconds to a blue of great beauty and intensity. These colours, like those to be mentioned presently, evidently depend upon oxidation, and would require a very large amount of material to follow out in detail. When the solution of hydriodate of æthyle-chinoline is heated on the water-bath with excess of oxide of silver, a volatile product is evolved, acting strongly upon the eyes.

Action of Sulphate of Silver upon Hydriodate of Æthyle-chinoline.

If hot solutions of sulphate of silver and hydriodate of æthyle-chinoline are mixed, double decomposition ensues, without any further action taking place, the solution of sulphate of æthyle-chinoline remaining colourless, and the iodide of silver separated being of the normal tint; but if it be attempted to concentrate the solution by evaporation on the water-bath, it undergoes a curious metamorphosis, the sides of the dish where the solution has dried become a deep pure blue, but as the evaporation proceeds the solution becomes crimson, and when dry the mass is so deep in tint as to be nearly black. The dry substance has a slight coppery lustre, like that which indigo possesses when rubbed. It dissolves in water, the solution being of the most gorgeous crimson, becoming rose-coloured by addition of ammonia, while hydrochloric or nitric acids convert it to a scarlet. The colour is tolerably stable, requiring a considerable excess of bromine-water to decompose it, the fluid then becoming reddish-brown.

The crimson liquid undoubtedly contains the sulphate of a new base, apparently a product of oxidation of æthyle-chinoline. The reactions upon which this supposition is founded are the following:—If solution of potash be added to the crimson solution, the colouring matter is almost entirely precipitated; and if the experiment be successful, the solution merely retains a slight blue tinge. This precipitate appears to be the new base, although probably in a very impure state. When first thrown down, it has a beautiful reddish-violet colour, like that of the crystallized sesquichloride of chromium. It may be washed with water on a filter, being sparingly soluble; it dissolves readily in alcohol, forming a fine crimson fluid, which precipitates a spirituous solution of chloride of mercury. The base dissolves readily in hydrochloric acid, the solution giving a voluminous precipitate with bichloride of platinum. The platinum-salt, after well washing with water, was burnt for the per-centage of metal, to ascertain whether its atomic weight was higher or lower than that of æthyle-chinoline.

2·081 grs. of platinum-salt gave 0·492 gr. of platinum.

212·2	157·0
Atomic weight of new base.	Atomic weight of æthyle-chinoline.

The atomic weight which is derived from this experiment is so excessively high, that no simple relation is apparent between the red product and æthyle-chinoline. The single platinum determination, although carefully made, is evidently insufficient to enable any speculation to be made as to the nature of the decomposition.

It is known that most nitryle bases (those composed solely of the alcohol radicals being the chief exceptions) yield colours by the action of oxide of silver on the ammonium compounds formed with methyle, æthyle, and amyle, but I think none yet worked on yield such magnificent tints as those mentioned in this paper. The subject has another and much greater point of interest than the mere formation of coloured reactions, however beautiful they may be, inasmuch as the careful following out of the decompositions on the large scale promises to assist us in acquiring a knowledge of the constitution of alkaloids of this class. I have therefore promised myself to examine the matter more fully, when the other investigations with which I am now occupied are concluded.

Action of Iodide of Amyle on Chinoline.

Hydriodate of Amyle-chinoline.—Iodide of amyle reacts with comparative slowness upon chinoline. It is necessary to keep the materials in a pressure-tube for some hours at 212° to effect combination. The iodide crystallizes from alcohol with extreme readiness, and when evaporated slowly upon flat surfaces presents under the lens very peculiar and beautiful forms.

The hydriodate of amyle-chinoline gave, in a determination of the per-centage of iodine, 38·75; the formula $C^{28} H^{18} N I$ requires 38·84.

The fluid from which the iodine had been precipitated was treated with hydrochloric acid in excess, the chloride of silver removed by filtration, and the fluid evaporated to a moderate bulk; excess of bichloride of platinum was then added, and the precipitated platinum-salt washed, first with a little water, and then with a mixture of alcohol and æther. The platinochloride of amyle-chinoline is only sparingly soluble in water; it was dried at 212°, and burnt with chromate of lead and copper-turnings:—

Carbon	41·31	28	=	168	41·43
Hydrogen........	4·63	18		18	4·44
Nitrogen	..	1		14	3·45
Chlorine	..	3		106·5	26·26
Platinum	24·24	1		99	24·42

Action of Chlorine on Chinoline.—According to Gerhardt*, chlorine converts chinoline into a black resin; but my experiments show that it acts in a very different manner if care be taken to prevent rise of temperature. On dropping chinoline into a large glass vessel of the gas, and leaving it for twelve or fourteen hours, a yellow oil is produced, which on treatment with water leaves a white insoluble matter, which I have not yet had an opportunity of studying more in detail.

Action of Chloride of Acetyle on Chinoline.—Chloride of acetyle, on being added to chinoline, developes much heat, and on evaporation at 212° a crystalline mass was obtained, but so deliquescent as to be unfit for examination.

On the Chinoline Series as it occurs in Coal-tar.

In my paper "On some of the Basic Constituents of Coal-naphtha and on Chrysene," I ventured to express a belief that chinoline was not the only member of the group to which it belongs present in coal-tar; and feeling assured that other homologues remained to be discovered, I was desirous of testing the accuracy of the supposition. Owing to the kindness of Mr. George Miller of

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* Traité, troisième partie, p. 150.

Dalmarnock, I was enabled to obtain 50 gallons of coal-oil of a very high boiling-point, and of a density greater than that of water. It was shaken with sulphuric acid to extract the alkaloids, and the acid fluid, after dilution with water, was treated with excess of lime, and distilled as long as any came over. As the amount of bases of the Dippel series present was not large, the product being of such a high boiling-point, I did not add potash to separate the more soluble portion, but only collected that part which, from its density and insolubility, sank to the bottom of the fluid accompanying it in the distillation. By means of a tap-funnel the basic oil was separated from the chief part of the water accompanying it, which contained some of the pyridine series in solution. The bases thus obtained are exceedingly impure, and contain aniline and some non-basic substances. It being probable that toluidine, and even other members of the same series, might be present, I thought that as apparently insurmountable difficulties prevented their separation from the chinoline series by means of oxalic acid, or similar methods, their presence might nevertheless be made manifest through their products of decomposition. With this view I treated the mixed bases with nitrite of potash and hydrochloric acid, in the manner indicated by Hunt*, and by this means effectually decomposed all traces of the aniline group present. But the amount of oil heavier than water containing the hydrates of phenyle and cresyle was too small to allow of my further examining them. I propose however to return to the subject at a future time.

The acid fluid, after decantation from the heavy oil last alluded to, was then placed in a retort, and a jet of steam sent through the tubulature to the bottom of the liquid; by this means many non-basic impurities were removed, and amongst them a white crystalline solid distilled over with the steam, and which eventually proved to be naphthaline. The acid fluid in the retort, after being filtered through pulverized charcoal, to separate resinous matters not volatilized, was treated with potash, to liberate the base, which was then separated by a tap-funnel, and completely dried by digestion with sticks of potash. It is proper to mention, that by this treatment the boiling-point of the bases was considerably raised, the aniline being removed, which boils 100° below chinoline.

The bases, as purified by the above method, yield on distillation fractions from 350° to 525°. Considerably more than one hundred distillations were made before sufficient separation had taken place to justify me in making any analyses.

Chinoline having already been proved to exist in coal-tar, I began the experiments by searching for lepidine. This base, which was discovered by me† among the volatile alkaloids procured by distilling cinchonine with potash, has the formula $C^{20} H^9 N$, which was established by analyses of the platinum-salt, nitrate, hydrochlorate, and bichromate, confirmed also by a determination of its vapour density.

As obtained from coal-tar, lepidine is in the form of an oil, having an odour almost exactly the same as that from cinchonine. But it is impossible by distillation alone, even after the treatment of the crude base with nitrous acid, to procure it in the same state as from the source where it was first found. Coal-lepidine therefore yields salts which for the most part crystallize with incomparably greater difficulty than that from cinchonine. When dissolved in an acid, although the solution is perfect, there is always an after-odour evolved, somewhat like naphthaline, unless the base has been purified with great care. I was unable, by any means at my disposal, to obtain the bichromate in a crystalline state, whereas the lepidine from cinchonine yields a beautiful salt in brilliant yellow needles half an inch long. Even when coal-lepidine is boiled with diluted chromic acid for an hour, the base, when separated and redistilled, gives an oily precipitate with chromic acid; moreover, the same occurs if the base be dissolved in hydrochloric acid, and a solution of bichromate of potash is added, as has been previously mentioned in describing the bichromate of chinoline. The red oil obtained in this manner from coal-lepidine may be kept for weeks without showing any tendency either to crystallize or decompose; even the base obtained from a platinum-salt of considerable purity behaved in the same way. On the other hand, coal-lepidine reacts with nitric acid and some other reagents like that from cinchonine.

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* Chem. Gaz., Jan. 1850.

† Trans. Royal Soc. Edinb., vol. xxi. pt. 27.

If it were not for the decisive manner in which the fact of Dr. Hofmann's having obtained the crystalline precipitate with leukole and chromic acid has been announced, I should have felt justified in asserting that the bases derived from the two sources were isomeric but not identical; but as the last-named chemist's well-known accuracy prevents me from entertaining a belief in the possibility of an error of experiment, I can only express my regret that I am ignorant of the method of purification adopted by him. The most satisfactory mode of explanation of the differences in the properties of the coal and cinchonine series, as obtained by me, is that they are in a peculiar molecular condition, analogous in some respects to the phænomena known in the cases of quinine, the amylic alcohol, and many other bodies, instances of which are daily becoming more numerous. Chemists are aware that even variations in the density and boiling-point of the same fluid, when in different states, have been observed; and I may mention, as corroborative of this, that with bases distilled the same number of times, lepidine, as pure as I could procure it from both sources, differed in boiling-point by 25° F.; for the lowest fraction of coal-lepidine that gave correct results on analysis distilled between 485° and 495°, whereas the lowest fraction of the same base from cinchonine boiled between 510° and 520° F. Another fact which seems corroborative of the supposition that Dr. Hofmann obtained the chinoline from coal-tar in the state in which I procured it from cinchonine, is found in the circumstance that the density of chinoline from coal-tar was ascertained by him to be 1·081, or very near the same number as in my determination of the density of the same base from cinchonine, viz. 1·085. But the coal bases examined by me were lighter than this, for even the lepidine from the last source had a density of only 1·072 at 60° F., being actually lighter than the homologue, one step below from cinchonine.

I have observed with the pyridine series, as obtained from bone-oil, coal-naphtha, and bituminous shale, that considerable differences are found in their power of forming crystalline salts, and it is therefore most probable that the same distinctions exist between them that are met with in the case of the bases from coal and cinchonine. I trust eventually to be able to elucidate some of these points by subjecting chinoline from both the above substances to the action of polarized light.

The lepidine platinum-salt from cinchonine precipitates at once in a pulverulent state; but from coal it is for a few seconds soft and resinous, but soon becomes hard and crystalline. The following are my analyses of it from the latter source:—

	I.	II.	III.	IV.	V.	Mean.			
C	34·48	..	34·58	..	..	34·53	20=	120	34·33
H	2·97	..	3·11	..	..	3·04	10	10	2·86
N	..	..	..	..	..	..	1	14	4·01
Cl	..	..	..	..	..	..	3	106·5	30·47
Pl	..	28·09	..	28·36	28·08	28·17	1	99	28·33

In the following table the mean of these results is compared with my analyses of the platinum-salt from the cinchonine bases:—

	Coal-tar. Mean.	Cinchonine. Mean.	Theory.
Carbon	34·53	34·04	34·33
Hydrogen	3·04	2·95	2·86
Nitrogen	..	..	4·01
Chlorine..........	..	..	30·47
Platinum	28·17	28·13	28·33

Action of Iodide of Æthyle on Lepidine.

Hydriodate of Æthyle-lepidine.—As it was evident that the process for preparing this compound, and from it the platinum-salt, was one of purification, I thought that I should by this means obtain nearer results on analysis than was the case with the experiments last quoted; and the following may be considered as confirming the truth of the supposition.

Coal-lepidine, sealed in a tube with excess of iodide of æthyle, and exposed for some hours to 212°, yields a mass of brown needles, which on recrystallization from alcohol are of a brilliant canary-yellow. They have the same property of becoming red at 212° as the corresponding salt of chinoline, although scarcely to the same degree.

7·111 grs. iodide of æthyle-lepidine gave 5·595 grs. iodide of silver=42·52 per cent. of iodine; the formula $C^{24} H^{14} N I$ requires 42·48.

Platinum-salt of Æthyle-lepidine.—This salt was obtained in the same manner as the corresponding one of æthyle-chinoline. It is, at the first moment of precipitation, somewhat soft, but soon becomes hard and crystallized. It was pulverized, and well washed with a mixture of alcohol and æther previous to analysis:—

	I.	II.	III.				
Carbon	38·00	..	..	24	=	144	38·14
Hydrogen ..	3·82	..	..	14		14	3·71
Nitrogen....	..	..	..	1		14	3·71
Chlorine....	..	..	..	3		106·5	28·21
Platinum....	..	26·47	26·60	1		99	26·23

Density of Vapour of Lepidine.—In my former paper on the chinoline bases I gave 5·14 as the density of the vapour of lepidine, as found by experiment; and I was desirous of ascertaining that of the same base, as extracted from coal-tar, in order to serve as a comparison. It is remarkable to observe the difference which an increment of $C^2 H^2$ has in modifying the power of substances to resist the decomposing influence of heat. While, in taking the density of chinoline at 531° F., being 71° above its boiling-point, the fluid condensed in the balloon was almost colourless, lepidine, after exposure under the same circumstances to only 523° F., or 28° above its boiling-point, had become nearly black; this darkening, caused by separation of carbon, prevented me from making the experiment at a temperature as much above the boiling-point as in the case of chinoline, and the two sources of error have the effect of making the density come out somewhat too high:—

Temperature of air	15° C.
Temperature of vapour....	273° C.
Pressure	755 millims.
Capacity of balloon	331 cub. centims.
Excess of weight of balloon	0·6745 grm.
Residual air	6 cub. centims.
Density	5·15

The formula $C^{20} H^9 N$ requires the following numbers:—

20 vols. carbon vapour....	=0·8290	.	20=	16·580
18 vols. hydrogen........	0·0692	.	18	1·2456
2 vols. nitrogen	0·9713	.	2	1·9426

$$\frac{19·7682}{4} = 4·94205$$

Density of vapour of lepidine from cinchonine.	Density of vapour of lepidine from coal.	Theory. $C^{20} H^9 N = 4$ vols.
5·14	5·15	4·94

On Cryptidine, a new Volatile Alkaloid homologous with Chinoline.

In examining the highest fractions of the bases from coal-tar, I have ascertained the presence of a new volatile base, to which I have given the above name. The quantity at my disposal was so exceedingly small, that the platinum-salt is the only compound I have been able to obtain in a state of tolerable purity; but the analyses of this substance leave no doubt whatever of the constitution of this the third homologue of the chinoline series.

If a solution of bichloride of platinum be added to a solution in hydrochloric acid of the fraction boiling about 525°, a pasty yellow mass precipitates, and on stirring adheres to the rod. In a few seconds the precipitate becomes crystalline, and is no longer adhesive, and if it is now dissolved in boiling water, it separates on cooling in groups of yellow needles, sparingly soluble in cold water. Two specimens of salt prepared in this manner, and well washed, first with water, and afterwards with a mixture of alcohol and æther, yielded on combustion the numbers following:—

	I.	II.	III.	IV.	Mean.			
C	35·83	..	35·95	..	35·89	22	=132	36·31
H	3·45	..	3·28	..	3·37	12	12	3·30
N	..	..	..	..	..	1	14	3·85
Cl	..	..	..	..	..	3	106·5	29·30
Pl	..	27·12	..	27·23	27·18	1	99·0	27·24

If the fraction boiling at 515° to 525° is treated with ordinary nitric acid, it dissolves with a purple coloration; and if the solution is evaporated to dryness and redissolved in water, an insoluble yellow powder becomes apparent. To the filtered solution, bichloride of platinum being added, an adhesive precipitate is formed having the properties previously assigned to the platinochloride of cryptidine as obtained from coal-tar. On solution in boiling water and subsequent cooling, a fine crop of orange-yellow needles was obtained, which, on combustion with chromate of lead and copper-turnings, gave the result annexed:—

		Calculation.
Carbon	36·51	36·31
Hydrogen	3·44	3·30
Nitrogen........	..	3·85
Chlorine........	..	29·30
Platinum........	27·25	27·24

A very perceptible increase in the carbon is therefore obtained by the removal of the impurity rendered insoluble by means of nitric acid.

Chinoline is therefore the first of a series of homologous nitryle bases, of which three members are now known, viz.

Chinoline	$C^{18}H^{7}N$
Lepidine	$C^{20}H^{9}N$
Cryptidine	$C^{22}H^{11}N$

And of which a greater number might possibly be obtained by an extension of the inquiry.—*Transactions of the Royal Society of Edinburgh*, vol. xxi. part 3.

On the Salts of the Sesquioxide of Manganese. *By* L. Carius.

For the production of sesquisulphate of manganese, the author employed artificially prepared brown oxide of manganese, made by passing chlorine through a solution of carbonate of soda, in which protocarbonate of manganese was suspended. This, when perfectly dry, was triturated with concentrated sulphuric acid until a thin paste was produced. A pound of this black mass was then heated on the oil-bath. Oxygen was evolved, but as soon as the paste had acquired the temperature of 230° F., all evolution of oxygen ceased, and the hitherto fluid mass became pasty and acquired a violet-gray colour. As the temperature rose to 239°–244° F., the mass became darker again, until at 270° F. it acquired a dark green colour and again became fluid.

The green colour arises from a compound which is insoluble in sulphuric acid, but which is suspended in the mass. The sulphuric acid filtered from it through asbestos contains only traces of dissolved sesquioxide of manganese.

The green body is exceedingly decomposable; with water, and more slowly by attracting moisture from the air, it lets fall brown hydrated sesquioxide of manganese. On the other hand, it may be washed with nitric acid if free from nitrous acid. Instead of filtering it through asbestos, which cannot be effected because the powder stops the openings of the latter, the mass is put upon plates of pumice-stone such as are sold for polishing, then stirred up with nitric acid, and again put upon the plates. When this process has been repeated six or eight times, the compound is pure. It is then put into a porcelain cup previously heated to 266° F., and heated as long as nitrous vapours are given off. It then retains no nitric acid. This green compound is the

Sesquisulphate of Manganese, $Mn^2O^3, 3SO^3$.—It forms a dark green powder, which may be heated by itself to 320° F. without losing oxygen. When boiled with sulphuric acid, it is converted into protosulphate of manganese. It is insoluble in concentrated sulphuric and nitric acids. In concentrated muriatic acid it dissolves, like pure sesquioxide of manganese, with a brown colour; and this solution only evolves chlorine when heated, and continues until the oxide of manganese is completely reduced to protoxide. With organic substances it behaves like a mixture of oxide of manganese and sulphuric acid. When organic matters are heated with the dry salt, the action is far more violent, so that when the heat is rapidly applied the mass sometimes ignites and is thrown about.

Sesquisulphate of manganese absorbs moisture from the air with extraordinary avidity, so that it can only be kept for any length of time in sealed tubes. Small quantities of the salt deliquesce in a few seconds, forming a clear, violet, cohesive fluid, which however becomes as quickly brown and turbid from the separation of hydrated sesquioxide of manganese.

With rather larger quantities the violet solution is not formed, but they are converted at first into a black crumbly mass, and afterwards become brown. If the salt be mixed with a large quantity of hydrated sulphuric acid and a little water, its green colour becomes converted into reddish-brown, without the occurrence of complete decomposition even with the aid of heat, or the solution even of small quantities of the salt in sulphuric acid. The reddish-brown powder exhibits very different properties according to the dilution of the sulphuric acid. It is a basic salt, and sesquioxide of manganese therefore behaves in this respect very like peroxide of iron, only that the salt is more easily decomposed by water, and at length forms acid and hydrated oxide. This behaviour therefore may be made use of to obtain pure hydrated sesquioxide of manganese. Thus all that is necessary is to heat finely divided superoxide of manganese (artificially prepared is the best) with concentrated sulphuric acid. If water be then added to this, a hydrated sesquioxide of manganese, free from all other oxides, is obtained. The analyses of the two bodies are as follows:—

1. **Sesquisulphate of manganese.**

Mn^2O^3	39·80	1	39·75
SO^3	60·19	3	60·25

2. **Hydrated sesquioxide of manganese.**

Mn^2O^3	89·51	1	88·64
HO	10·49	1	11·36

Such hydrated oxide of manganese combines at 212° F. with sulphuric acid, without any evolution of oxygen, forming green sesquisulphate of manganese. Dilute sulphuric acid does not dissolve any of it either in the cold or with the assistance of heat; but if the hydrate contains intermixed protoxide, some of the former also dissolves with a violet colour. If pure sesquioxide of manganese be mixed with about double its quantity of protoxide of manganese, and dilute sulphuric acid be poured over the mixture, nearly all the sesquioxide of manganese dissolves even in the cold, forming a deep red fluid. The solubility of the sesquisulphate of manganese in dilute sulphuric acid therefore appears to depend on the formation of double salts, although the author did not succeed in obtaining any such salt in a crystalline form.

This explains why the solution of sesquisulphate of manganese is usually obtained red; for a hydrated sulphuric acid, if not perfectly concentrated, evolves oxygen with peroxide and sesquloxide of manganese until the excess of water is driven off. Protoxide of manganese must therefore always be formed, and this is the cause of the production of a red solution when it is diluted with water.—Liebig's *Annalen*, xcviii. p. 53.

On two new Methods for the Artificial Formation of Urea.

By J. NATANSON.

The opinion has been repeatedly put forward, that the chemical behaviour of urea agrees with that of a hypothetical amide of carbonic acid; but as urea could not be prepared in the same way as the amides, and as it generally forms compounds which, according to the number of equivalents, contain a double atom of carbamide, the question of the constitution of urea has remained unsettled.

The author thinks that the following experiments furnish a complete proof of the identity of carbamide and urea.

If carbonate of oxide of æthyle be treated with ammonia in a sealed tube at 212° F., uræthane only is formed; but if the temperature be raised to the boiling-point of uræthane, or about 356° F., it is converted into urea by the action of the excess of ammonia. A sublimate of undecomposed uræthane is formed in the empty part of the tube; the aqueous solution contains urea. If this solution be evaporated to dryness and kept at 212° F. for some time, the uræthane is volatilized, and the residue is pure urea, as may be recognized at once by its reaction with nitric acid. To get rid of the whole of the uræthane, the urea thus obtained is washed with æther.

This urea crystallized from its aqueous solution in acicular columns, from its alcoholic solution in laminæ; it was very soluble in water and alcohol, and insoluble in æther; its fusing-point was 241° F.; its taste was cooling, and nitric and oxalic acids produced abundant crystalline precipitates in its solutions. The nitrate of urea could be obtained by recrystallization in well-formed, characteristic, rhombic prisms. By the precipitation of the oxalic acid from the oxalate of urea by chloride of calcium, and the conversion of the oxalate of lime into carbonate and then into sulphate, the following results were obtained:—

	Found.	Calculated.	
1 equiv. anhydrous oxalic acid......	47·42	36	48·00
1 equiv. urea	..	30	40·00
1 equiv. water	..	9	12·00

In a determination with chloride of barium in Bunsen's way, a portion of the fluid was accidentally lost in opening the sealed tube; but the decomposition of the urea into carbonate of baryta and muriate of ammonia was observed.

In 1838, Regnault, in his experiments upon the action of phosgene gas upon ammonia*, obtained a white saline mass, which behaved like a mixture of carbamide and muriate of ammonia; he was unable, however, to separate the carbamide from the muriate of ammonia. But as the aqueous solution of this mixture was not precipitated by nitric acid, Regnault concluded that no urea was contained in the mixture, and that carbamide and urea were distinct. Nevertheless the author says true urea does exist in this white mass. The principal condition of success in this experiment is, that the two gases shall be as dry as possible, and the difficulty of realizing this condition is the cause that the urea is usually formed in small quantity in proportion to the muriate of ammonia, so that it cannot be detected by the reaction with nitric acid, which requires rather concentrated solutions.

The author prepared his phosgene gas by Hofmann's method†, by passing carbonic oxide through boiling perchloride of antimony, and he found this process very convenient. The two gases were conducted into a dry spacious balloon. By the extraction of the mass thus obtained with absolute alcohol, evaporating the alcoholic extract to dryness, dissolving it in a little cold water, and adding nitric acid, the presence of urea may be detected; nitrate of urea is separated at all events in the course of a few hours. The whole of the urea may be obtained by adding an excess of baryta-water to the white mass to decompose the muriate of ammonia, drying it under the air-pump over sulphuric acid, and extracting the urea with absolute alcohol. The alcoholic solution is again evaporated, and the residue dissolved in water; any traces of baryta are precipitated by carbonate of ammonia, and the urea is then thrown down from its concentrated aqueous solution by nitric acid. The removal of the baryta is indispensable, as nitrate of baryta is difficult of solution even in an excess of nitric acid; the excess of carbonate of ammonia goes off for the most part during evaporation, and its presence is not injurious to the reaction, as nitrate of ammonia is very soluble in nitric acid. The nitrate of urea thus obtained was separated from the acid fluid, and dried with blotting-paper; when recrystallized from its aqueous solution, it formed beautiful rhombic tables. Nitric acid instantly produced a white precipitate in the aqueous solution of these crystals. The crystals were dissolved in concentrated sulphuric acid, and the gas evolved during heating passed through a bulb-apparatus with baryta-water; an abundant white precipitate was immediately formed, which dissolved with effervescence in acetic acid, and as the urea prepared from the nitrate by carbonate of potash and subsequent extraction with alcohol agreed with ordinary urea in its taste, crystalline form, and solubility, the author considered that an analysis might be dispensed with.—Liebig's *Annalen*, xcviii. June 1856, p. 287.

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* Ann. de Chim. et de Phys., lxix. p. 180.

† Liebig's Annalen, lxx. p. 139.

Chemical Investigation of the Blood. By J. SCHERER.

Some years since the author made an examination of the blood in leucæmia, and found some remarkable bodies in the filtrate from the coagulum. Besides a body presenting all the reactions of gluten and setting into a perfect jelly, there was a second body, standing between albumen and the gelatine group; and lastly, a considerable quantity of hypoxanthine, which occurs normally in the spleen, and lactic, formic, and acetic acids.

The blood, in the present case, after standing for some time, presented a marbled mixture of black and red on the surface exposed to the air, although in a less degree than that previously examined. When boiled with water, however, it did not coagulate so completely as in the former case, so that the addition of a drop of acetic acid was necessary for the complete separation of the albuminous bodies and of the red colouring matter.

The filtrate thus obtained was brought to the consistence of a thin syrup on the water-bath, and left to stand for some days after cooling. It did not exhibit the least tendency to a gelatinous congelation, from which the absence of gluten was inferred. The addition of alcohol to a portion of it gave rise to no turbidity. On the other hand, a small quantity of a yellowish-white pulverulent precipitate had been formed at the bottom of the evaporating dish. This was purified by decantation of the fluid, filtration, and washing with cold water; and to test it for hypoxanthine, a small portion of it was placed with nitric acid on platinum foil and evaporated. As soon as the fluid was dried, the pale yellow residue of nitrohypoxanthine was formed, but at its edges there was an intense red colour, such as uric acid usually produces with nitric acid.

Under the microscope, however, no crystals of uric acid could be detected. The whole mass consisted of extremely fine granules, such as are always observed in hypoxanthine. As however the reaction of uric acid had appeared so distinctly with nitric acid that there could be no doubt of its presence, the author proceeded to separate it from the hypoxanthine by the process which he had previously employed in the examination of the spleen. He treated the yellow powder with caustic ammonia, by which the hypoxanthine was easily and completely dissolved, whilst the uric acid remained undissolved. The portion remaining undissolved (about ½ gr.), when evaporated with nitric acid and mixed with ammonia, gave the murexide reaction with remarkable beauty. The ammoniacal solution of hypoxanthine, left to spontaneous evaporation, furnished about 2 grs. of a pure residue, presenting the beautiful reactions of hypoxanthine with nitric acid and potash.

The fluid decanted from the yellow deposit of uric acid and hypoxanthine was further evaporated, and a small portion of the fluid, when concentrated as much as possible, was left to evaporate spontaneously under the microscope. There appeared an abundance of crystals of chloride of sodium, and round clear globules, with a not very distinct outline; these dissolved on the addition of water, and were also readily soluble in ammonia, and after spontaneous evaporation again appeared in the well-known forms of clear globules and pyriform grains, such as are furnished by pure leucine under the same circumstances.

For greater certainty the fluid was evaporated to the consistence of a thick syrup, dissolved in a small quantity of water, and filtered; absolute alcohol was then added to the filtrate, when the leucine was deposited on the walls of the glass in a crystalline form. When separated from the mother-liquor and the slimy deposit at the bottom of the glass, again dissolved in water, and left to spontaneous evaporation under the microscope, it again furnished the crystalline globules above described.

The alcoholic solution poured away from the leucine reduced nitrate of silver with the assistance of heat, indicating the presence of formic acid. The greater part of the silver salt added was however thrown down as chloride of silver.

To the remainder of this fluid small quantities of concentrated sulphuric acid were added as long as they produced a white turbidity. The fluid was separated from the sulphates by decantation and filtration, and boiled with carbonate of lime. The filtrate from this, when evaporated to dryness and dissolved in boiling alcohol, gave, on the addition of æther, crystals of lactate of lime, which were converted into carbonate of lime by calcination.

Thus in this blood again several of the soluble constituents of the parenchyma of the spleen were detected, namely, hypoxanthine, uric acid, lactic acid, leucine, and formic acid. It was not tested for acetic acid, as a small quantity of this was employed in the coagulation of the blood, and its detection therefore appeared to be superfluous.—*Verhandl. der Phys.-med. Gesellsch. zu Würzburg,* 1856, p. 123.

On the Decoloration of Silk and Wool dyed Yellow with Picric Acid. By C. Pugh.

According to Pugh, silk, wool, &c., dyed with picric acid, do not change their colour by immersion in a hot solution of protochloride of tin or iron, although these are both very energetic reductive agents. But if, after washing, they are immersed in an alkaline solution, a red colour is produced in consequence of the formation of hæmatin-nitric acid; but this colour dissolves, and the stuff remains almost white. Perhaps by using certain mordants this would furnish a means of fixing red patterns upon yellow grounds. —*Journ. für Prakt. Chem.*, lxv. p. 368.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of Phosphoric Acid. By Dr. W. Reissig.

Reynoso, finding that tribasic phosphoric acid is completely thrown down from the nitric acid solution of its salts by metastannic acid, founded an excellent method of determining phosphoric acid upon this circumstance. As the compound formed has no definite composition, he recommends to combine the phosphoric acid with a known quantity of metastannic acid, and to ascertain the amount of phosphoric acid by the increase of weight. For this purpose he puts a weighed quantity of pure tin into the concentrated solution of the phosphate, and deducts from the weight of the compound obtained after calcination that of the metastannic acid which corresponds with the tin employed.

This method presents certain difficulties which limit its applicability. It is very difficult to obtain perfectly pure tin. The purest occurring in commerce, even the best tin foil, contains copper, lead, iron, &c. Even by oxidizing the metal with nitric acid, and subsequently reducing the metastannic acid, it is scarcely possible to get rid of these impurities completely, as metastannic acid so obstinately retains traces of other metallic oxides, that these are with difficulty extracted from it by nitric acid. As besides at least eight times as much tin foil must be employed as there is phosphoric acid present, the error arising from the impurity of the tin is multiplied nearly eight times. Again, metastannic acid is not absolutely insoluble, and the loss which the large precipitate undergoes in the treatment with nitric acid and washing, goes with the other errors to make a loss of phosphoric acid in the determination. Reynoso's method however is quite inapplicable when, as is often the case, besides the phosphate, chlorides or similar substances are present, as these, by their reducing action upon the metastannic acid, will give rise to the formation of soluble chloride of tin or protosalts of tin, and thus cause a considerable loss. By the author's process, the investigations for which were carried on in Bunsen's laboratory and at his instigation, the phosphoric acid is again separated from the metastannic acid, and determined directly as phosphate of ammonia and magnesia.

The substance to be examined is dissolved in concentrated nitric acid, the requisite quantity of tin foil is added to it, and it is heated for five or six hours until the precipitate has entirely settled. It is then washed by decantation, the washing-water being allowed to run through a filter. The precipitate is then poured into a platinum capsule, and digested for some time with a small quantity of very concentrated solution of potash, by which it is converted into metastannate and phosphate of potash, which readily dissolve to form a clear fluid on the addition of hot water, especially when the hydrate of potash was not in too great excess. The small quantity of precipitate collected on the filter is treated in the same way and added to the first solution, and the whole fluid is then saturated with sulphuretted hydrogen, a little pentasulphuret of ammonium is added to it, and it is mixed with acetic acid until the sulphuret of tin is precipitated and the fluid has a slightly acid reaction. Too much acetic acid retains a portion of tin in the solution, and the fluid cannot be filtered clear. In separating the precipitate from the solution of phosphoric acid by filtration, a small quantity of tin is always dissolved during the washing of the slimy precipitate, whether this be done with cold or hot water, pure or containing sulphuretted hydrogen. When the filtered fluid is evaporated, the addition of ammonia almost always separates a small portion of a compound containing stannic and phosphoric acids, which causes a loss of phosphoric acid. In three experiments performed in this way, the fluid, when precipitated by an ammoniacal solution of magnesia, gave 32·04, 31·74, and 31·60 per cent. instead of 32·99 per cent. of phosphoric acid.

To avoid this loss and the troublesome washing of the precipitate, the author proposes the following method. The precipitation is effected in a large weighed glass flask, in which the fluid is diluted with so much water as to weigh about 1000 grms. When it is uniformly mixed in the flask by shaking, this is weighed again with its contents, and the precipitate is allowed to settle as completely as possible, which usually takes from twelve to sixteen hours. The clear portion of the fluid is filtered into an evaporating vessel, and evaporated to a small volume, and the phosphoric acid contained in it is determined in the usual way as phosphate of ammonia and magnesia. The flask with its remaining contents is then weighed again, to get the weight of the fluid poured away; the tin precipitate is collected on a weighed filter, washed, dried, and weighed. The filtrate and the washing-waters are not further employed. The weight of the precipitate need only be determined roughly, as an error of half a gramme is of no consequence.

Let g be the weight of the empty flask, g^1 its weight with its contents before the removal of the portion of fluid serving for the determination of the phosphoric acid, g^2 its weight after this fluid has been poured away, p the weight of the filtered sulphuret of tin, and p^1 that of the calcined pyrophosphate of magnesia obtained from the portion of the fluid poured off; then the whole weight of the fluid containing phosphoric acid is

$$g^1-g-p,$$

and the weight of the portion used in the determination of the phosphoric acid is

$$g^1-g.$$

The amount of phosphoric acid contained in the whole of the fluid P is therefore

$$P=\frac{PO^5(g^1-g-p)p^1}{2(MgO),PO^5(g^1-g^2)}.$$

If the quantity of fluid g^1-g be so great that the weight of the precipitate of sulphuret of tin is only from $\frac{1}{1000}$ to $\frac{1}{500}$ of it, p may be calculated without any perceptible error from the weight of the tin employed, instead of determining it directly by a troublesome filtration.

To test the method, a solution containing muriatic acid, sulphuric acid, peroxide of iron, alumina, magnesia, and lime was mixed with various quantities of a phosphate of soda, the amount of phosphoric acid in which had been determined by two concurrent experiments at 21·58 per cent., and the phosphoric acid was determined by the method described. The experiments gave—

Experiment.	PO^5 employed.	PO^5 found.	Difference.
1.	0·0430	0·0432	+0·0002
2.	0·0909	0·0913	+0·0004
3.	0·1287	0·1275	−0·0012
4.	0·0659	0·0635	−0·0024
5.	0·0781	0·0756	−0·0025

The same experiments, repeated with a pure solution of the phosphate of soda of known value, gave—

Experiment.	PO^5 employed.	PO^5 found.	Difference.
6.	0·0485	0·0492	+0·0007
7.	0·4233	0·4228	−0·0005
8.	0·7752	0·7740	−0·0012

Liebig's *Annalen*, xcviii. June 1856, p. 339.

PATENTS.

Patent for Improvement in the Manufacture of Cast Iron, by David Simpson Price, Ph.D., Consulting Chemist, 2 South Molton Street, Middlesex, *and* Edward Chambers Nicholson, Manufacturing Chemist, 3 Newington Crescent, Surrey.

THE object of the invention is to produce a cast iron of a quality adapted for purposes where great strength is required, such as for the manufacture of ordnance, girders, &c.

The invention is based upon the principle that there exists a relation between the strength of cast iron and its chemical composition, and relates especially to reducing the quantity of silicon, as being the impurity which tends most to diminish the strength of cast iron.

In order to lower the per-centage of this impurity, the patentees employ the product of the refinery process known as *metal*, which they find to be free from silicon, and to contain an amount of carbon not very much less in quantity than that existing in the gray pig iron from which it is obtained, but to be present in the combined instead of the graphitous state. This (*metal*) is to be melted, together with good qualities of gray pig iron, in proportions which experience may point out as the best for certain purposes.

In manufacturing *metal*, the operation of refining is not to be carried on for a longer period than is necessary, in order that as little carbon as possible may be lost.

No alteration is required in the present mode of smelting iron, attention being directed to the varieties of ores which it is desirable to employ, with a view of preventing the pig iron being unnecessarily charged with impurities. These embrace the ores smelted in this country. A preference is given to iron smelted by cold blast.

By carrying out the above principle, it is shown that when pig iron and *metal* (both obtained by the use of coal) are employed, that cast iron of the composition of that hitherto produced only by the use of charcoal can be manufactured; whilst if a mixture of charcoal products is in like manner made, a cast iron of very great purity will be the result.

The principle of the invention being that which is alone claimed, no preferences are given as to the methods for carrying out the mixing.

It is stated that either gray or mottled iron can be produced as required.—Sealed May 20, 1856.

Patent for Improvement in the Manufacture of Cast Steel, by the same.

In this process the fact of *metal** containing the whole of its carbon in the combined state, or that in which it exists in steel, is rendered available; and the invention consists in mixing with *metal* the necessary quantity of wrought iron, to reduce the per-centage of carbon to the proper amount, and thus to produce cast steel.

The patent refers to iron and *metal* obtained from cast iron smelted by coal.—Sealed May 20, 1856.

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* See patent for cast iron.

THE CHEMICAL GAZETTE.

No. CCCXXXII.—August 15, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Nitric Oxide Gas upon Anhydrous Sulphuric Acid. By A. BRÜNING.

VERY different opinions are held as to the constitution of the compounds formed by the different oxides of nitrogen with sulphuric acid. The statements with regard to the action of nitric oxide gas upon that acid are especially contradictory. It is now completely settled that nitric oxide gas does not form any compounds with hydrated sulphuric acid, but its behaviour with anhydrous acid is not so certainly known. H. Rose obtained a compound by passing dry nitric oxide gas into a balloon, the walls of which were coated with anhydrous sulphuric acid, and from which the air had been expelled by an indifferent gas. He attributes the formula $2SO^3, NO^2$ to the compound produced; it was amorphous, but crystallized after fusion, and furnished nitric æther with alcohol, which does not agree with the supposition that it contained nitric oxide. Kœne, referring to this reaction, contradicts the statements as to the formation of the body, and says that in this way he could obtain nothing but a sulphuric acid contaminated with a little nitrous acid.

With the view of ascertaining exactly the behaviour of nitric oxide gas towards anhydrous sulphuric acid, the author put some of the latter into a dry flask, expelled the air with carbonic acid gas, and then filled the flask with nitric oxide gas, after contracting its neck a little. It was then carefully sealed up, the sulphuric acid was diffused by the action of heat, and brought into complete contact with the nitric oxide, and the flask was again opened. The access of the air produced only a slight brown colour of hyponitric acid at the point, but the greater part of the nitric oxide gas had disappeared. On the other hand, the odour of sulphurous acid was distinctly perceptible. This gas could only have been formed from the sulphuric acid, which had furnished 1 equiv. of oxygen to the nitric oxide to form NO^3 (or NO^4), which had then entered into combination with the sulphuric acid. This was proved to be the case, for when the sulphurous acid was expelled by carbonic acid, the decomposition of the substance by a little water gave red fumes of NO^3 or NO^4, with previous production of a blue colour.

In the following experiments the author used straight tubes of

4 to 5 decims. in length and 15 millims. in internal diameter, drawn out at both ends. In these he sublimed the sulphuric acid repeatedly, and passed through them carbonic acid, until the gas passing off ceased to decolorize a fluid coloured blue by iodide of starch, which it did at first in consequence of the presence of a small quantity of sulphurous acid in the sulphuric acid. Dense fumes were produced immediately on the introduction of the nitric oxide gas into these tubes; these probably arose from the extremely volatile compound of sulphurous and sulphuric acids. When the tubes, after nitric oxide had long passed through them, were sealed up at both ends, heated for a long time and then again opened, the water through which the products were driven with carbonic acid presented the odour and reactions of sulphurous acid in a high degree. When the tubes were opened under water, the latter rushed in violently, and was again driven out by the gases evolved. These experiments therefore prove that nitric oxide abstracts oxygen from a portion of the anhydrous sulphuric acid, forming nitrous or hyponitric acid, which combines with the remainder.

To determine the quantity of sulphurous acid set free by this reaction, the experiment was repeated with this variation, that the perfectly pure sulphuric acid was sealed up in a small tube, the empty portion of which was filled with carbonic acid, and this was put into a larger tube and broken by shaking, after the latter was filled with nitric oxide gas and sealed up. This enabled the amount of nitric oxide employed to be determined.

The tube contained 56 cub. centims. The nitric oxide gas, measured at 59° F. and reduced to 32° F., gave 53·09 cub. centims., representing 0·07103 grm. The sulphurous acid gas was expelled by carbonic acid and passed through a flask with water, then through a glass tube filled with wet glass, and lastly into a solution of iodine of known strength. 50 cub. centims. of a solution, each containing 0·0053 grm. of iodine, were employed. The excess of iodine was removed by 50 cub. centims. of a solution of sulphurous acid, and the excess of this determined by 11·8 cub. centims. of solution of iodine. 50 cub. centims. of the aqueous sulphurous acid represented 13·8 cub. centims. of the solution of iodine. The sulphurous acid produced therefore took 48 cub. centims. of the solution of iodine, containing 0·2544 grm. of iodine, which corresponds with 0·0641 of sulphurous acid. Calculation gives 0·0757 grm. of sulphurous acid, supposing 1 equiv. of nitric oxide to set free 1 equiv. of sulphurous acid; but as the latter may not all have been expelled by the carbonic acid, the result is sufficiently close to show that nitrous acid, and not hyponitric acid, is formed. The compound therefore consists of sulphuric and nitrous acids.

To obtain it in a state fit for analysis, the greatest care must be taken to employ both the sulphuric acid and the nitric oxide in a perfectly dry state, which is a matter of great difficulty with the latter. This may be the reason why so many have failed in preparing the solid compound, as a small quantity of water is sufficient to hold it dissolved in hydrated sulphuric acid. The sulphuric acid was put into a U-shaped tube, united with another by plaster of Paris. The latter was intended for the reception of the sulphuric acid, which is strongly volatilized, especially at the beginning of the experiment. If the operation be properly conducted, scarcely anything but sulphurous acid passes through the outlet-tube. The temperature must be constantly raised, and towards the end, when nearly at the boiling-point of the compound, nitric oxide gas is passed through.

For analysis, a portion of the substance was fused and kept in well-closed tubes.

The analysis gave—

	Found.	Calculated.
$2SO^3$	68·41	67·79
NO^3	30·91	32·21

Thus the action of nitric oxide upon anhydrous sulphuric acid may be expressed by the following equation:—

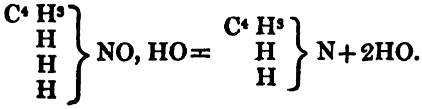
$$3SO^3+NO^2=(2SO^3, NO^3)+SO^2.$$

The melting-point of the compound is 422°·6 F. Its point of solidification could not be exactly determined, as it remained long transparent, and only became perfectly opake at 368° F. When fused, it is reddish-yellow; when more strongly heated, it gradually becomes darker, until at a high temperature it is volatilized. Water decomposes it immediately, and when exposed to the air it continually attracts water and gives off NO^3, until at last it becomes fluid.

Its reactions agree with those described by H. Rose, and there is no doubt that De la Provostaye also obtained the same body* by bringing fluid hyponitric acid in contact with fluid sulphurous acid. But whether this compound contains NO^3 combined with $2SO^3$, or whether, as De la Provostaye thinks, 1 equiv. of sulphuric acid forms a conjugate compound with another in which 1 atom of oxygen is replaced by 1 atom of NO^4, cannot easily be proved by experiment.—Liebig's *Annalen*, xcviii. June 1856, p. 377.

Researches on Acetylamine. *By* J. NATANSON.

The author has already stated†, that oxide of acetylammonium, when heated, gives off vapours with a characteristic odour resembling the organic ammonias; by dry distillation, to discover the substance to which this odour is due, he found that at a high temperature oxide of acetylammonium is simply decomposed into acetylamine and water,—



$$\left.\begin{matrix}C^4H^3\\H\\H\\H\end{matrix}\right\}NO, HO=\left.\begin{matrix}C^4H^3\\H\\H\end{matrix}\right\}N+2HO.$$

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* Journ. für Prakt. Chem., xxi. p. 401.

† Liebig's Annalen, xcii. p. 48.

Oxide of acetylammonium may be easily obtained pure by evaporating the yellow fluid produced by the action of chlorelayle and ammonia until the muriate of ammonia crystallizes, separating the mother-liquor from the crystals, and evaporating this to dryness with an excess of hydrate of baryta. The evaporation is tedious, as the tough mass only gives off the last portions of water slowly at 212° F. The dry hard residue is put into a glass balloon, and extracted with absolute alcohol, which dissolves the oxide of acetylammonium, and the alcoholic extract is evaporated to dryness without access of carbonic acid. Traces of baryta may be thrown down by careful addition of sulphuric acid. The base thus obtained forms a pale yellow inodorous mass.

The alcoholic solution of the base is put into a retort, and the alcohol and any traces of water are distilled off. The temperature is then raised, and at 302° F. watery drops again begin to pass over; these have an alkaline reaction, possess a very weak ammoniacal taste, and consist of water containing very small quantities of acetylamine. The decomposition therefore commences at 302° F., but at first it is principally the produced water that passes over, whilst the acetylamine, possessing a very high boiling-point, remains in the retort. When the watery distillate becomes scanty, the temperature is raised to 428° F., when yellow oily drops pass over, consisting of nearly pure acetylamine. When the heat is raised above 428° F., the distillate becomes more or less brown, but may be easily purified by a single rectification. At a temperature of 482° F. other products of decomposition appear to be formed, and the amount of acetylamine obtained is small; so that, in order to avoid a considerable loss, the temperature must by no means be allowed to rise above 428° F., although the distillation often lasts for hours. It is best to employ an oil-bath so deep that the greater part of the retort may be covered with hot oil, as otherwise a good deal remains adhering to the walls of the retort; but even under these circumstances a small carbonaceous residue in the retort can hardly be avoided. To rectify it, it is put into a dry retort, and heated for a long time to 302° F., to make sure that all traces of water are driven off; the temperature is then quickly raised, and the portion passing between 410° and 428° F. collected separately in a dry receiver. The pale yellow fluid thus obtained proved to be pure acetylamine, $\left.\begin{matrix}C^4H^3\\H\\H\end{matrix}\right\}N$. Its analysis gave,—

C	55·97	4	=	24	55·81
H	11·31	5		5	11·63
N	32·26	1		14	32·56

Analyses of the platinum double salt gave,—

	Found.			Calculated.	
C^4H^5N,HCl	..	..	..	79·50	31·92
2Cl	..	..	..	71·00	28·57
Pt	39·34	39·29	39·86	98·56	39·51

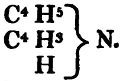
Pure acetylamine is a very pale yellow fluid; it is probably colourless in its purest state. It has a peculiar, ammoniacal, persistent odour. At ordinary temperatures this is rather weak, and resembles that of aldehyde-ammonia; but the vapours of boiling acetylamine have an odour like that of perfectly pure aniline. At ordinary temperatures it is a rather thick fluid; when heated it becomes constantly thinner. Its boiling-point is 424°·4 F. At 59° F. its specific gravity is 0·975, and it does not become solid at −13° F. Its vapour burns with a bluish-white flame. It mixes with water and alcohol in all proportions, but not with æther. It has *no action* upon dry litmus-paper, although it soaks into it; on the access of water the paper soon becomes deep blue. Its taste is caustic; when applied to the skin, it renders it rather slippery. In contact with fused globules of sodium at the ordinary temperature, not the least action takes place.

Acetylamine combines with acids with evolution of heat, forming salts which possess all the properties of the salts of oxide of acetylammonium described by the author. When the sulphate is prepared, thrown down from its aqueous solution by alcohol, and decomposed by solution of potash, the characteristic odour of acetylamine is not reproduced. The acetylamine is therefore separated in the form of the inodorous oxide of acetylammonium. It is very slowly converted into oxide of acetylammonium by water, and aqueous solutions of acetylamine long retain their peculiar odour. Acetylamine attracts water and carbonic acid from the air, and then effervesces with acids. A glass rod moistened with muriatic acid and held over acetylamine, produces strong white fumes. The density of the vapour of acetylamine was found to be 1·522; calculation for a density of 4 vols. gives 1·505.

Acetylamine behaves as follows towards metallic salts. Lime- and baryta-salts are not precipitated by its aqueous solution. Magnesia-salts give a white precipitate, which is insoluble in an excess of the precipitant. Zinc-salts give a white precipitate, which readily dissolves in an excess of the base. Salts of alumina also give a white precipitate, which is insoluble in an excess of acetylamine. In copper-salts its aqueous solution produces a pale yellow precipitate, which is not completely dissolved by an excess of the base, but acquires an azure-blue colour; this precipitate is not altered by boiling. Lead-salts give a white precipitate, but only when heated. Persalts of iron give a brown precipitate, insoluble in an excess of the precipitant. In salts of nickel, acetylamine produces a blue precipitate, which becomes red by boiling. Silver-salts give a white precipitate, which dissolves very readily in an excess of the base, but is decomposed, with reduction of silver, by the least heat. Bichloride of mercury gives a white precipitate, which dissolves readily in an excess of base. Bichromate of potash is converted into the neutral salt by acetylamine; its red colour is instantaneously rendered pale yellow. The aqueous solution of acetylamine is not precipitated by tartaric acid, tannic acid, or sulphocyanide of potassium. Tartrate of copper and potash is not reduced by acetylamine, even when boiled. The salts of oxide of acetylammonium, when heated with solution of chloride of lime or with chromate of potash and sulphuric acid, evolve aldehyde as abundantly as in the reaction previously described by the author with nitrite of silver*.

Perchloride of platinum and acetylammonium ($C^4H^5N, HCl + PtCl^2$), when freshly precipitated, forms an orange-yellow amorphous powder; this is rather difficult of solution in cold water, but dissolves readily in hot water, and is nearly insoluble in alcohol and æther. It is precipitated by alcohol from its aqueous solution. When this precipitate is dissolved in a little hot water, the platinum-salt separates on cooling in the form of a crystalline powder, which is a mixture of very fine needles and the amorphous double salt. The salt separates even from dilute aqueous solutions when left to evaporate slowly, forming crystalline crusts, which consist of druses of the needles above mentioned.

Derivatives of Acetylamine.—If acetylamine be heated with iodide of æthyle, it is converted into a brown, semisolid, transparent mass, which is an iodide of the æthylized base. This iodide dissolves in water, and hydrate of potash separates a brown oil from this solution; this is soluble in alcohol and æther, attracts carbonic acid from the air, and forms compounds with acids, which however could not be obtained crystallized. From the solution of this oil in muriatic acid, perchloride of platinum throws down an amorphous tile-red powder. The brown oil is probably æthylacetylamine,



$$\left.\begin{matrix}C^4H^5\\C^4H^3\\H\end{matrix}\right\}N.$$

When aniline is treated with chloride of elayle in sealed tubes at 392° F., the mixture becomes deep blood-red. If the tubes be opened after a few hours, a considerable portion of the fluid dissolves in water, whilst chloride of elayle and aniline alone are nearly insoluble in that fluid. The aqueous solution contains muriates of aniline and acetylaniline. If it be now precipitated by solution of potash, a mixture of oily drops of aniline and a pale brown precipitate of acetylaniline is obtained; this is soon decomposed by the potash, becoming darker, and then changing its colour to red and violet. The aniline may be separated from the acetylaniline by ammonia, which precipitates the former. The yellow ammoniacal solution is then evaporated to dryness, and the muriate of acetylaniline extracted with absolute alcohol. The alcoholic solution is again evaporated, the reddish-yellow salt dissolved in a little water, and the acetylaniline precipitated by baryta-water. The yellowish-brown precipitate must be quickly filtered, as the long action of the excess of baryta-water decomposes it in the same way as solution of potash. The acetylaniline thus obtained, when washed with water, forms a pale, brown, tasteless, and inodorous powder, which is readily soluble in alcohol, but insoluble in water and æther. When the alcoholic solution is evaporated, it does not crystallize, but remains as a shining, brittle, brown mass. It dissolves in acids with a yellowish-red colour. When heated with nitrate of silver and

* Liebig's Annalen, xcii. p. 54.

ammonia, it gives a silver speculum; with nitrite of silver it evolves an abundance of aldehyde. Nitrate, sulphate, muriate, and oxalate of acetylaniline dissolve in water and alcohol, but remain as uncrystallizable masses on evaporation. Perchloride of platinum throws down the platinum double salt from the solution of the muriate in the form of brownish yellow flakes. This salt is pretty soluble in hot water, but separates as an amorphous powder on cooling. The precipitate, washed with water and alcohol, gave the following numbers on analysis:—

	Found.		Calculated.	
1 equiv. muriate of acetylaniline ..	..	..	155·50	47·83
2 equivs. chlorine	..	..	71·00	21·81
1 equiv. platinum	30·09	29·66	98·56	30·36

Acetylaniline has therefore the formula $\left.\begin{matrix}C^4\,H^3\\C^{12}\,H^5\\H\end{matrix}\right\}N$, and its mode of formation may be expressed as follows:—

$$\underset{\substack{\text{Chloride of}\\\text{elayle.}}}{C^4\,H^4\,Cl^2}+\underset{\text{Aniline.}}{2C^{12}\,H^7\,N}=\underset{\substack{\text{Muriate of}\\\text{aniline.}}}{C^{12}\,H^7\,N,\,HCl}+\underset{\substack{\text{Muriate of}\\\text{acetylaniline.}}}{C^{16}\,H^9\,N,\,HCl.}$$

The compounds representing the amides were also formed from acetylamine. If butyric æther be mixed with an alcoholic solution of oxide of acetylammonium or with pure acetylamine, and heated, the whole sets into a jelly of fine acicular crystals. These are not butyrate of acetylamine, but an acetylamide of butyric acid, $\left(C^8\,H^7\,O^2+\left.\begin{matrix}C^4\,H^3\\H\end{matrix}\right\}N\right)$, as butyrate of acetylamide does not crystallize, but forms a tough yellow mass, and butyric acid does not produce a precipitate either in an alcoholic solution of oxide of acetylammonium, or in pure acetylamine, and when butyric æther is mixed with acetylamine the odour of alcohol is perceptible.

The author considers that the comparison of acetylamine and oxide of acetylammonium furnishes an important contribution to the ammonium theory. The decomposition into the corresponding ammonia and water only takes place here at 302° F., whilst with the ordinary oxide of ammonium it probably takes place far below 32° F. The constitution of the two bases however is the same, and it is to be hoped that some chemist may yet succeed in obtaining many hitherto hypothetical oxides of ammonium in an undecomposed state at a low temperature. Acetylamine possesses all the properties of the ammonias, such as volatility, odour, capability of combining with acids, &c.; but it has no reaction upon dry litmus-paper, although it moistens it. With water and acids it forms compounds corresponding to the so-called ammoniacal salts, but at the same time loses its peculiar character, as it is separated by stronger bases in the form of solid, inodorous, strongly alkaline oxide of acetylammonium. These facts, the author thinks, give a further support to the opinion already expressed by him, that the ammonias are only *neutral* products of decomposition of the oxides of ammonium, which represent peculiar bases.

Cloëz, in his notice of the action of bromide of elayle upon alcoholic solution of ammonia*, has described the formylamine which he obtained by the distillation of the resulting bromide with potash-lime, and which boils between 280° and 289° F., but he has scarcely mentioned acetylamine. The formation of formylamine in this case may perhaps be due to the decomposition of oxide of acetylammonium by hydrate of potash; and the author, by using alcohol of spec. grav. 0·863, instead of absolute alcohol, in the preparation of oxide of acetylammonium, by which means a considerable quantity of baryta was dissolved, obtained a far smaller amount of acetylamine, whilst in the first distillation a base was formed the sulphate of which was crystalline. Its analyses and that of its platinum-salt led to results which approached more closely to the formula of formylamine than to that of acetylamine. With pure oxide of acetylammonium, no other base but acetylamine was obtained. On the other hand, it is possible that the formation of formylamine may depend upon the accidental presence in the chloride or bromide of elayle of the compound $C^2H^2Br^2$.—Liebig's *Annalen*, xcviii. June 1856, p. 291.

On Sulphobenzide. *By* H. GERICKE.

In 1834, Mitscherlich discovered a crystallizable body, produced by the action of the anhydride of sulphuric acid upon benzine. It received the name of sulphobenzide, and was regarded as a compound of the hydrocarbon benzide with sulphurous acid ($C^{12}H^5+SO^2$). Gerhardt doubled its formula, and derived it from the hydrogen type, in which 1 equiv. H is displaced by the radical sulphophenyle, and the other by the radical phenyle, thus: $\left.\begin{array}{l}C^{12}H^5S^2O^4\\C^{12}H^5\end{array}\right\}$.

At the instigation of Prof. Limpricht, the author has studied this body, and now communicates some of his results, promising a more complete account of his investigations in a short time.

He considers the rational formula of sulphobenzide to be $\left.\begin{array}{l}C^{12}H^5SO^2\\C^{12}H^5SO^2\end{array}\right\}$, so that it would be a so-called radical, containing in 1 atom 2 equivs. of the radical $C^{12}H^5SO^2$. If it had the formula proposed by Gerhardt, it would probably be decomposed by potash into sulphophenylate of potash and benzine, thus:

$$\underset{\text{Sulphobenzide.}}{\left.\begin{array}{l}C^{12}H^5S^2O^4\\C^{12}H^5\end{array}\right\}}+KHO^2=\underset{\substack{\text{Sulphophenylate}\\\text{of potash.}}}{C^{12}H^5KS^2O^6}+\underset{\text{Benzine.}}{C^{12}H^6}.$$

It does not however undergo the least change when heated for several hours to 356° F. with concentrated alcoholic solution of potash.

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* Institut, xxiii. p. 243.

When heated with sulphuric acid, it is converted into sulphophenylic acid, as already described by Mitscherlich:—

$$\underset{\text{Sulphobenzide.}}{C^{24}H^{10}S^{2}O^{4}} + S^{2}H^{2}O^{8} = \underset{\text{Sulphophenylic acid.}}{2C^{12}H^{6}S^{2}O^{6}}.$$

The behaviour of sulphobenzide towards nitric acid shows the necessity for the duplication of Mitscherlich's formula, $C^{12}H^{5}SO^{2}$, which indeed is indicated by the equivalents of hydrogen and sulphur not being divisible numbers. When it is heated for some time with fuming nitric acid, water throws down a yellow product from it, and this is decomposed by hot alcohol into nitrosulphobenzide and binitrosulphobenzide.

Nitrosulphobenzide, $\left.\begin{array}{l}C^{12}H^{4}(NO^{4})SO^{2}\\ C^{12}H^{5}\qquad\quad SO^{2}\end{array}\right\}$, is readily soluble in hot alcohol, and separates on cooling in a soft honey-yellow mass, which becomes solid in the cold; by the spontaneous evaporation of the alcoholic solution, small undefined crystals are obtained, which are soluble in æther but not in water, fuse at 294° to 298° F., and are decomposed at 482° F. Sulphuret of ammonium converts nitrosulphobenzide into a base by the introduction of amide in place of the hyponitric acid.

Amidosulphobenzide, $C^{24}H^{9}(NH^{2})S^{2}O^{4}$, separated from its muriate by potash, consists of microscopic four-sided prisms, which are difficult of solution in cold water, but dissolve readily in hot water and alcohol, fuse when heated, and afterwards become decomposed. The *muriate*, $C^{24}H^{9}(NH^{2})S^{2}O^{4}$, HCl, forms well-developed four-sided prisms, which dissolve in water and alcohol, and fuse at about 294° F. Perchloride of platinum produces a yellowish-brown precipitate in the concentrated solution; this is $C^{24}H^{9}(NH^{2})S^{2}O^{4}$, HCl, $PtCl^{2}$, and shows no distinct crystals under the microscope. The author has not ascertained to which group of bases amidosulphobenzide belongs; it is probably an imide base, and the formula might be written $N\left\{\begin{array}{l}C^{12}H^{5}SO^{2}\\ C^{12}H^{5}SO^{2}\\ \quad H\end{array}\right.$. Gerhardt's formula would express amidosulphobenzide as sulphophenylanilide, $N\left\{\begin{array}{l}C^{12}H^{5}S^{2}O^{4}\\ C^{12}H^{5}\\ \quad H\end{array}\right.$.

Binitrosulphobenzide, $\left.\begin{array}{l}C^{12}H^{4}(NO^{4})SO^{2}\\ C^{12}H^{4}(NO^{4})SO^{2}\end{array}\right\}$, is obtained in the largest quantity by employing a mixture of sulphuric and nitric acids. The precipitate produced with water when recrystallized from alcohol forms silky, microscopic, rhombic tables, which are difficult of solution in hot alcohol and æther, fuse at 327° F., and are sublimed without decomposition above 608° F. Sulphuret of ammonium converts it into *biamidosulphobenzide*, $C^{24}H^{8}(NH^{2})^{2}S^{2}O^{4}$, which is thrown down by potash from its solution in nitric acid as a yellowish-white precipitate, which soon becomes brown. It dissolves readily in hot, and with difficulty in cold water, and crystallizes in small four-sided prisms. The muriate, $C^{24}H^{8}(NH^{2})^{2}S^{2}O^{4}$, 2HCl, crystallizes in four-sided rhombic prisms, in the solution of which perchloride of platinum produces a brownish-red indistinctly crystalline precipitate of the composition $C^{24}H^{8}(NH^{2})^{2}S^{2}O^{4}$, 2HCl, $PtCl^{2}$. The rational formula of biamidosulphobenzide must also be settled by further experiments; it is probably a binacid base,

$$N^{2}\left\{\begin{array}{l}C^{24}\,H^{8}\,S^{2}\,O^{4}\\ \quad H^{2}\\ \quad H^{2}\end{array}\right. ,$$

for which the platinum-salt $$N^{2}\left\{\begin{array}{l}C^{24}\,H^{8}\,S^{2}\,O^{4}\\ \quad H^{2}\\ \quad H^{2}\end{array}\right. ,\ 2HCl,\ PtCl^{2}$$

especially speaks, as this, allows of no division into $$N\left\{\begin{array}{l}C^{12}\,H^{4}\,SO^{2}\\ \quad H\\ \quad H\end{array}\right. .$$

—Liebig's *Annalen*, xviii. June 1856, p. 389.

On the Atomic Weight of Antimony. *By* H. Rose.

The correction of the atomic weight of antimony by Schneider is a point of such importance, and one which must so essentially change the views entertained as to the composition of many antimonial compounds, especially the salts of antimonic acid, that it appears desirable that this determination should be confirmed as soon as possible.

Shortly after the appearance of Heffter's paper on the composition of the antimoniates, the author induced Weber to make some experiments on the atomic weight of antimony, in the expectation that perhaps a more correct determination of this might lead to an essential simplification of the complicated formulæ which Heffter had been compelled to adopt from the atomic weight established by Berzelius.

For this purpose the fixed chloride of antimony, $SbCl^{3}$, was decomposed by sulphuretted hydrogen, and the amount of chlorine determined as chloride of silver. It appeared, as the author had already indicated, that the precipitated sulphuret of antimony could not be entirely freed from chlorine by washing with water, without the employment of tartaric acid. But by using this, the weight of a double atom of antimony was established at 1508·67, which nearly agrees with the number 1503, deduced by Schneider from his experiments.

Thirty-one years ago the author had analysed the two chlorides of antimony, also with the aid of tartaric acid. By calculating the atomic weight of antimony from the results then obtained, we get for the weight of a double atom the numbers 1513·04 and 1508·5. —*Bericht der Akad. der Wiss. zu Berlin,* 1856, p. 239.

ANALYTICAL CHEMISTRY.

On the Detection of Iodine, especially in the Presence of Reducing Agents. *By* Dr. W. Knop.

Liebig has recently described an excellent method for the detection of small quantities of iodine, founded on the oxidation of iodine by the addition of iodic acid, $5HI+IO^{5}=5HO+I^{6}$.

I had occasion to seek for iodine in a fluid which contained much sulphurous acid. Here therefore iodic acid could not be employed, as it would be reduced by the sulphurous acid, and thus the iodine purposely added would be found.

Liebig's method however may be easily adapted to such cases, which was of importance to me, as I had some years ago been occupied in the discovery of a method which might serve for the bromizing of organic bodies by determinable quantities of bromine. This process consists in adding a solution of bromate of potash from a burette containing 1 grm. of bromate of potash in 100 degrees of water to a mixture of the organic substance with an excess of hydrobromic acid, and calculating the quantity of bromine from the number of centigrammes of bromate of potash employed. The decomposition is the same as the above, $5BrH + BrO^5 = 5HO + Br^6$. For the removal of the excess of bromine, which by its yellow colour serves to indicate the saturation, I employed hyposulphite of soda in a second burette. When these two processes are combined, bromate of potash furnishes a second oxidizing agent for hydriodic acid.

To 2 litres of water I added a drop of solution of iodide of potassium, 1 grm. of sulphite of soda, a little starch and sulphuric acid, left it standing for an hour at the ordinary temperature, and then added bromate of potash. As soon as this was in sufficient quantity for the complete oxidation of the sulphurous acid, it was added very carefully at intervals of five to ten minutes.

The blue colour is seen to be produced with peculiar intensity. Heat, the light of the sun, and even very bright diffused daylight, must be avoided. As a matter of course, the iodine compound may be destroyed by a great addition of bromate of potash; but by operating as above described, and adding the bromate of potash in a very dilute solution, the reaction is gradually produced, and a point is always first attained at which the starch becomes intense blue, this colour being only destroyed again by an excess of the bromate.

The state of dilution in which iodine is still discoverable by bromate of potash is perfectly extraordinary; and it appears to me that bromate of potash is to be preferred to all the other oxidizing agents, except perhaps iodate of potash.

Perhaps the quantitative determination of extremely small quantities of iodine may be effected by the employment of an arrangement similar to Müller's complementary colorimeter, by reading off the height of a complementarily-coloured column of fluid which exactly cancels the blue colour. An extremely dilute solution of bichromate of potash furnishes a good complementary colour to the blue of iodine, and may be employed for this purpose.—*Chemisches Centralblatt*, 32, July 9, 1856, p. 497.

On the Influence of Muriatic Acid upon the Precipitation of some Metals by Sulphuretted Hydrogen. By M. Martin.

From solutions strongly acidified with muriatic acid, lead, antimony, silver, copper, bismuth, tin, mercury, and cadmium are not precipitated. When much diluted with water, the precipitation is total. The quantity of muriatic acid which prevents precipitation is different for different metals. The smallest is required by lead; the others require a larger quantity in the proportion indicated by the following sequence, Cd, Sb, Sn, Hg, Bi, Cu, Ag. Silver requires rather more muriatic acid than is necessary to hold the chloride in solution. When the muriatic acid present is not sufficient to hold the metal completely in solution, sulphuretted hydrogen precipitates a portion of it. This behaviour might therefore be made use of to ascertain the quantity of muriatic acid necessary for the solution of metals.

A. *Determination of the Quantity of Muriatic Acid for Lead.*

1. 0·230 grm. of acetate of lead were dissolved in 80 cub. centims. of a solution containing 2·5 per cent. of muriatic acid. The employment of such weak acid was necessary with lead, in order to bring the chloride of lead into solution. The quantity of lead employed, calculated as chloride of lead, gives 0·168 grm. The quantity of chloride of lead remaining dissolved after the passage of sulphuretted hydrogen (precipitated by oxalate of ammonia, and weighed as oxide of lead) was 0·005 grm., amounting to 2·976 per cent. of the chloride of lead employed.

2. Quantity of acetate of lead, 0·115 grm.=chloride of lead, 0·084 grm. The chloride of lead remaining dissolved after treatment with sulphuretted hydrogen amounted to 0·0024 grm., or 2·857 per cent. of the substance employed. These experiments therefore show that the action of the muriatic acid is not affected by the quantity of the chloride.

B. *Determination for Copper.*

1. 0·5 grm. of sulphate of copper were dissolved in 40 cub. centims. of muriatic acid of spec. grav. 1·13. The acid contained in this was therefore 10·5 grms., and the quantity of chloride of copper 0·269 grm. Of this, 0·034 grm. remained in solution =12·639 per cent. of the substance employed.

2. 0·5 grm. of sulphate of copper were dissolved in 54 cub. centims. of muriatic acid of spec. grav. 1·095. The acid contained in this was therefore also 10·5 grms., and the quantity of chloride of copper 0·269 grm. Of this, 0·009 grm. remained in solution, making only 3·345 per cent. of the whole.

The author has also found that the reducible metals, which are retained in solution by muriatic acid, are reduced by sulphuretted hydrogen to the lowest oxide. Solution of perchloride of copper loses its green colour, and the solution contains protochloride of copper. In the same way the perchlorides of mercury and bismuth are converted into protochlorides, during which process free sulphur is deposited. With perchloride of mercury, sulphur and protochloride of mercury are thrown down together. The protochloride of bismuth produced has the formula $BiCl^2$.

The author has called attention to this behaviour of muriatic acid, especially because Spirgatis, in his memoir upon the separation of zinc from copper, has recommended the strong acidification of the solution of the two metals by muriatic acid, in order to prevent the imperfect separation observed by Biot and Bouquet.—*Journ. für Prakt. Chem.*, lxvii. p. 371.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Colouring of Metal Wares. By A. O. MATHEY.

IN Switzerland, the galvano-chromic process has been for some time employed in colouring different parts of watches, and this has induced the author to institute a series of experiments upon this mode of colouring metals, the foundation of which consists in covering a metallic surface with an extremely thin coat of oxide, which then produces certain colours like those produced in the tempering of steel.

The galvanic apparatus employed by the author is a small permanent battery of two pairs; the electrodes and conducting wires are of iron or platinum. The oxides which the author has hitherto made use of as colouring agents are peroxide of lead and peroxide of iron.

Preparation of the Lead Solution.—425 to 450 grms. of caustic potash are dissolved in a litre of distilled water, about 125 grms. of oxide of lead (massicot is the best) are added, and the mixture is boiled for ten minutes in a flask with a narrow neck, so that there may be as little access of air as possible. After cooling, the solution is decanted from the oxide of lead remaining undissolved, and diluted with distilled water until it shows 24° to 25° B., this density being the most proper to furnish fine colours. It is kept in a well-closed bottle, so that no foreign matters may have access to it. As the solution is used, carbonate of potash is gradually formed in it. It is then boiled with caustic lime, and left to settle, and the clear fluid is again employed. From time to time it must be boiled with oxide of lead. When this solution is employed for colouring objects which exhibit rough spots, they do not acquire a uniform colour. The author considers the probable cause of this to be, that the fluid does not conduct the electricity so well as the metal; and this defect can easily be got rid of by increasing the conducting power of the fluid by the addition of an acid. For this purpose bitartrate of potash is often added; but this, according to the author, is the least fitted for the purpose, and may be much better replaced by oxalic acid, acetic acid, &c. It is best however to add no acid at all, as its addition greatly injures the solidity of the colour, and the object may also be obtained without it. For this purpose massicot is better than litharge, as it dissolves more readily in potash. It may be prepared, when this is necessary, by heating minium in an unglazed earthen pot to a dull red heat, and constantly stirring it with an iron rod until a sample of the mass exhibits a citron-yellow colour on cooling. Too strong a heat must be avoided, as this would fuse the oxide.

Preparation of the Iron Solution.—Although this solution presents difficulties in its preparation and employment, it may still frequently be made use of, and is even indispensable in some cases, as it furnishes tints which cannot be obtained with solution of lead. Sulphate of iron, which possesses a pale green colour and has not begun to oxidize, is dissolved in warm distilled water; the solution is boiled to drive off all the air, and drawn off into a well-closed bottle. When it is to be used, the necessary quantity of it is poured out of the bottle, and mixed with ammonia free of air until the precipitate produced is again dissolved, which however does not take place completely unless an acid or an ammoniacal salt be added at the same time. The solution, thus prepared, cannot be employed for more than an hour, because peroxide of iron is thrown down from it by the action of the oxygen of the air. The colours obtained by means of this solution are much less changeable than those furnished by the lead solution. They are brighter, and as solid as the blue which is produced on steel by heating it.

Preparation of the Objects to be coloured.—The galvanic colouring is employed as much as possible for metallic surfaces which are not liable to oxidation, as the object must be attached to the positive pole; and when its surface consists of an oxidizable metal, it frequently loses its brightness. For the peroxide of lead separated from the lead solution, a golden, or gilt, or platinum surface furnishes the best recipient. On platinum it produces a beautiful blue, but on gold a green, owing to the colour of the metal shining through. On German silver and the other white metals, the green colour only appears after they have become blue. The colouring of silver does not take place in the same way as in the other metals, because it soon undergoes an oxidation, which renders its surface dull and prevents the appearance of the colour. The alloys which contain silver, even only in small quantity, do not colour well in consequence, and change rapidly, on which account silver must be carefully avoided in this process.

The goodness of the result depends especially upon the proper cleaning and preparation of the object. The better this is polished, the brighter will be the colour; a surface polished with a steel burnisher becomes more beautiful than one polished only with oxide of iron. Before colouring, each piece must be carefully cleaned, and especially freed from all fatty matter; for this purpose it is dipped into a solution of potash (an alcoholic solution is the best), and washed afterwards in water. For large articles chalk may also be employed. After cleaning, the objects must not be touched with the fingers, nor even with a cloth.

Mode of performing the Operation.—If we suppose that watch-hands are to be coloured, six pairs of them are put upon a steel rake, the teeth of which have the proper form and elasticity for fixing the hands with their prongs. The rake is put in connexion with the positive pole of the battery, and then immersed in the fluid. It must be covered by the latter to a depth of about 25 millims.; if it be immersed to a greater depth, the colours produced cannot so well be observed, and the desired tint is not so easily obtained. When all is thus arranged, the negative electrode is moved about in the surface of the fluid with only its point immersed. In the course of five to six seconds the watch-hands are seen to change; the first order of colours are allowed to pass, and when they become gray the second order begins. The gray disappears to give place to a yellow, which then also disappears, and is replaced by red. This moment requires every attention not to allow the desired tint to pass away; and in this respect it must be observed that the colours do not appear so deep in the fluid as they really are. When the hands appear red in the fluid, they are violet in reality. When they are to be red, they must be taken out when they appear orange in the fluid. If the tips of the hands acquire the desired colour sooner than the heads, the tips are lifted out of the fluid, whilst the portions which are not yet sufficiently coloured remain immersed; and the current is then allowed to act interruptedly, that is to say, the tip of the negative electrode is immersed repeatedly for a moment in the fluid until the desired colour is produced throughout. The duration of the operation varies from 10 to 40 seconds. It is advisable to treat a large number of watch-hands at once, as they then turn out more uniform in colour.

If the current be too strong, hydrogen and oxygen gases are evolved at the electrodes. The object then acquires a grayish appearance, and the iron electrode becomes covered with spongy lead. Under these circumstances the current must be weakened, and the operation commenced afresh after the object has been again polished. A brass plate of a certain size, when exposed to the action of the current, remains passive, and acquires no colour whatever. If this be the case, a small portion of the plate must first be immersed, and in proportion as it changes colour it must be further immersed. If the object be large, it infallibly acquires several colours, because the portions most distant from the point of connexion with the conducting wire are coloured most rapidly. This becomes of more importance the less the conducting power of the fluid. In order to do away with this inconvenience, the object must be united in several places with the positive pole, and the negative electrode must be allowed to run out in several wires suitably arranged. A fresh bath always produces several tints upon the same plate, and the bath improves by use. The hands placed upon the rake are therefore allowed to remain some minutes in the fresh bath, and then coloured in an old one. If the colour do not turn out well, the object is cleaned in strong vinegar, and then coloured again. In this way the object may be coloured two or three times without a second polishing, when it consists of gold of at least 14 carats. When a gilt object has been submitted to the colouring process five or six times, the gilding is entirely removed, so that it must be again gilt and polished. If a coloured object be brought in contact with the negative pole in the lead solution, its colour disappears, the peroxide of lead being dissolved. This method of removing the colour is preferable to the use of vinegar.

Production of various Colours on the same Object.—When an object, such as a bouquet of flowers for a brooch or hair-pin, is to be furnished with several colours, it must first, if it be not made of gold, be strongly electro-gilt, and deadened according to circumstances. Those portions which are to retain the colour of gold are then coated by means of a hair pencil with black varnish (*epargne noire liquide*), and the object is connected with the positive pole, and put into the lead-bath. When all the flowers have become pale red, those which are to retain this colour are also covered with varnish; the object is again immersed in the bath, and the other flowers allowed to become violet. Those which are to retain this tint may then be coated with the varnish, and the remainder may be allowed to become blue. When the latter are coated in the same way, another immersion will render the leaves green. The green may also be shaded, as at first a dark green appears, which becomes lighter, and finally passes to yellow. The varnish is removed by treatment with cold oil of turpentine, and the object is cleaned first with soap and water and a soft brush, and afterwards with warm water and a cloth. These various colours, which resemble the natural colours of flowers, and are deposited upon a ground of dead gold or silver, have a splendid effect, and in brilliancy and lustre leave the paintings on enamel far behind them; but they unfortunately do not possess the permanency of the latter. Single silver flowers with gilt stamina produce a pretty effect in such a bouquet.

Causes of the Change in the Galvanic Colours, and the means of preventing it.—Dry air produces no alteration whatever in the colours produced by peroxide of lead; but this is not the case with moist air, especially when it contains traces of sulphurous acid or sulphuretted hydrogen. On this account the colours of watch-hands are changed by the exhalations from the body, if the case of the watch is not perfectly air-tight. The author frequently observed, that of two pairs of hands which had been coloured under similar circumstances, the one had entirely changed its colour in eight days, whilst the other was completely unaltered after the lapse of a year. He long tried in vain to discover the cause of this, but is now convinced that the rapid change of colour was to be attributed to the presence of a trace of potash, under the influence of which oxide of lead was reproduced, and this combined with the potash. This last cause of the destruction of the colour may be easily guarded against by washing the object when coloured with boiling water, so that all potash is removed, wiping it, and drying it on a hot iron plate. With regard to the alteration of colour produced by the action of moist air and air charged with foreign matters, Becquerel has recommended the application of a protective varnish to the coloured objects. This varnish must have as little reducing action as possible, so as not to decompose the peroxide of lead. For this purpose Becquerel recommends the following varnish:—½ a litre of linseed-oil, 4 to 8 grms. of prepared litharge, and 2 grms. of sulphate of zinc are put into a glazed pot, and the mixture is heated moderately for some hours. The clear varnish is then decanted from the undissolved portion, and mixed, when it is too thick, with oil of turpentine, which must be previously boiled with oxide of lead to remove all traces of acid. The object is very thinly coated with this varnish by means of a hair pencil, dried by a gentle heat, and then coated a second time. By the application of this varnish, the colours, as Becquerel remarks, lose something of their lustre, and also appear partly of a different tint, but they gain in durability. According to the author's experiments, Becquerel's varnish is inapplicable, and every varnish applied over the red colours causes them to appear yellow. If the varnish be removed, the red colour appears again unchanged. The action of the varnish therefore does not depend upon a change of the peroxide of lead, but upon the alteration of the thickness of the stratum laid upon the metallic surface upon which the colour depends.—*Polyt. Centralblatt*, 1856, p. 612.

Note on the Oils employed in the Manufacture of Turkey-red.

By J. Pelouze.

All the fixed oils are not equally proper for the preparation of the dyes known under the names of Turkey-red and Adrianople-red. Those generally used are olive oils, distinguished by the name of emulsive oils (*huiles tournantes*), from the property which they possess of producing a milky emulsion with a weak alkaline solution. To distinguish them, the manufacturers let fall 1 or 2 drops of the oil into a test-glass partly filled with a solution of caustic soda marking 1½ to 2 degrees, and judge of the value of the oil by the greater or less opacity of the drops of oil. The oils proper for the manufacture of Turkey-red being expensive, it has been endeavoured to replace them by cheaper oils, mixed with yolk of egg, treated with nitric acid, &c., but without success, as the manufacture of Turkey-red still consumes great quantities of natural emulsive oils.

The author formerly showed* that if crushed oleaginous seeds were left to themselves, the neutral fatty bodies contained in them were changed into acids, and announced that these partially acidified oils would then shortly be applied in the manufacture of Turkey-red. He had ascertained that the oils used for that purpose were mixtures of neutral and acid fatty bodies; and by treating them with alcohol, found that they yielded portions of oleic and margaric acids varying from 5 to 15 per cent. The acids may also be extracted from the oils by heating them for a few minutes with an alkali. Ordinary olive-oil contains no fatty acids, or only an insignificant quantity of them.

The author's observations on the spontaneous saponification of fatty bodies easily explain the difference in the composition of these oils. The pure oils are obtained by the simple division and immediate pressure of the olives, whilst the treatment of the cakes and other residues, and the fermentation of the olives, cause the acidification of the oil, and render it emulsive (*tournante*).

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* Chem. Gaz., No. 301, p. 161.

For some years MM. Boniface of Rouen have prepared an artificial oil of this kind; and the author, on examining it, found it to contain considerable portions of oleic and margaric acids, but the process by which it is prepared is not known. However, it appears that the only difference between the two categories of commercial oils—those fitted for dyeing are mixed with fatty acids, whilst the others are free from them. M. Chevreul, also, more than twenty years ago, extracted two oily matters from Turkey-red stuffs; one of these was neutral to litmus, whilst the other reddened it, and was composed of oleic and margaric acids.

The author states that olive-oil has been almost exclusively employed in dyeing Turkey-red, because olives give rise to the reaction which produces the fatty acids more readily than the oleaginous seeds, and that it will be easy to substitute for it cheaper oils, such as poppy-oil, oil of sesame, colza-oil, palm-oil, &c. It will be sufficient to crush the seeds or kernels, and leave them for a short time before extracting the oil. A still more simple means consists in adding to the oils a few hundredths of their weight of the oleic and margaric acids furnished by the manufacturers of stearine candles. This last method has succeeded with M. Steiner of Manchester, and M. Pelouze also communicates a letter from MM. Henry of Bar-le-Duc, containing some useful information on the substitution of artificially acidified oils for those which are naturally acid, and exhibited to the Academy of Sciences specimens of cotton-dyed Turkey-red with both the natural and artificial oils, and between which there was no perceptible difference.

He adds, that it is very probable that the treatment of certain oils, especially colza-oil, with a little sulphuric acid, would give rise to mixtures of neutral oils and fatty acids, which when well washed would be fit for the manufacture of Turkey-red.

MM. Henry state that the quantity of oleic acid required to give the necessary properties to the oil varies according to the nature of the latter from 5 to 15 per cent., and they have even produced the effect with 2 per cent. The oils require to be purified to a certain extent. The cotton-dyed (10 kilogrms. of thread) gave a good tint, proportioned to the madder employed; the oil used was 3 kilogrms. of purified colza-oil with 60 grms. of oleic acid, or only 2 per cent. They are convinced that it will succeed on the large scale.—*Comptes Rendus*, June 23, 1856, p. 1196.

PATENT.

Patent granted to T. Petitjean, *for Improvements in silvering, gilding, and platinizing Glass.*

This invention consists in coating glass with solutions or products obtained by combining vegetable acids or hydracids (or these combined with chlorine, iodine, or bromine) with metallic salts of silver, gold, or platinum, the bases of which are combined with mineral acids or hydracids. (An alkali must be mixed with the metallic salt or with the vegetable acid.)

The following are examples of the manner of carrying the invention into effect:—

To silver Glass.—In order to silver glass, two solutions of silver are first prepared.

Solution No 1 is formed by combining 4 chemical equivs. of ammoniacal nitrate of silver with 1 equiv. of tartaric acid and a suitable quantity of distilled water. To 10½ oz. of nitrate of silver 6½ oz. of liquid ammonia are added. The ammonia being poured upon the nitrate of silver, the combination of the two takes place with a disengagement of heat. The mixture is stirred until the combination of the two is complete, and when left to stand for several hours, crystals of ammoniacal nitrate of silver are formed. To this solution 2½ pints of distilled water are added, and the whole is well stirred to assist the crystals to dissolve. The solution is then filtered to separate from it a small quantity of black powder which is formed during the combination of the nitrate of silver and the ammonia, and to the filtered liquid is added 1⅙ oz. of tartaric acid dissolved in 4 times that weight of distilled water. Subsequently 6 quarts of distilled water are added and stirred well, and the mixture is then to stand for decanting. Upon the precipitate of tartrate of silver, which is left after the decanting has taken place, from 7 to 8 quarts of distilled water are poured, in order to dissolve as much as possible of it. The solution is stirred and left to stand for a sufficient time, after which the liquor is decanted and mixed with the first solution. About 15 quarts of a solution of silver is thus obtained, to which 2 quarts of distilled water are added, in order to make it perfectly limpid. The solution is then quite ready for use. What remains of the precipitate of tartrate of silver after the liquid is the second time decanted from it is dissolved by means of a few drops of nitric acid, and laid aside.

Solution No. 2 is formed by combining 2 chemical equivs. of ammoniacal nitrate of silver with 1 equiv. of tartaric acid and a suitable quantity of distilled water. All the manipulations gone through in the preparation of this solution are the same as in the case of solution No. 1, the only difference between the two solutions being that the quantity of tartaric acid in No. 2 is double that in No. I. These solutions should be prepared for one day's use only.

The glass to be silvered should be well cleaned before it is operated upon. For this purpose a little of the solution No. 1 is used to moisten a piece of cotton, to which a little putty-powder is applied, and with this the surface of the glass is carefully rubbed, after which it is allowed to dry. The rubbing is then repeated with a little dry putty-powder, and when the glass is perfectly clean its face is damped with a roller covered with india-rubber, which is wetted with No. 1 solution. The glass is then laid upon a suitable apparatus heated to about 150° F., and upon it No. 1 solution is poured until the surface of the glass is covered with the liquid. In about fifteen or twenty minutes a thin coating of silver is seen to be deposited all over the surface of the glass, and then as much of No. 2 solution as the surface can retain is poured thereon. (The surface will retain about half a pint of the liquid on each square foot of it.) In about fifteen minutes (or twenty minutes at most) the coating of silver is so much increased in thickness by a deposit from the second solution, that it becomes opake. (One pennyweight of silver is thus deposited upon every square foot of the surface of the glass.) After removing from the glass the excess of the solution, the coating of silver is washed with warm water to cleanse the surface from any remains of the solution. It is then dried and coated with quickly-drying oil colour or brown varnish. In this manner a looking-glass is obtained incomparably finer, lighter, and more solidly coated than those made by the common process, and that too without in any way injuring the health of the operator*.

Glasses which are of such shapes that they cannot be cleaned by the process hereinbefore described, such as smelling-bottles for example, are first plunged into a strong solution of hyposulphite of soda, and left to lie in it for ten or twelve hours. They are then washed several times, and filled with solutions No. 1 and No. 2 successively.

It is not absolutely necessary to heat the glass, as the deposition from the solutions takes place at either high or low temperatures, but the action is quickened with an increase of heat, and *vice versâ.*

To gild and platinize Glass.—The operations hereinbefore described, in reference to the silvering of glass, are repeated in the gilding and platinizing of glass, with no other alteration except that a change is made in the solutions employed, the solutions of silver being replaced by solutions of gold and platinum respectively, and that one solution of gold and one of platinum only are needed.

Solution of Gold.—This solution is formed by combining 2 chemical equivs. of perchloride of gold with 1 equiv. of citrate of ammonia. In a quart of distilled water 1 oz. of chloride of gold is dissolved, and the mixture filtered; to this is added a mixture of 10½ drms. of citric acid previously dissolved in 4 or 5 times its weight of distilled water, with 5½ drms. of liquid ammonia. This solution of gold should not be prepared until it is required for use.

Solution of Platinum.—This solution is formed by combining 1 chemical equiv. of perchloride of platinum with 1 equiv. of bitartrate of soda. In a quart of distilled water dissolve 1 oz. of chloride of platinum, and filter the mixture; then add to it 13 drms. of bitartrate of soda previously dissolved in 8 or 9 times its weight of distilled water, and after well stirring the whole the solution is ready for use.—Dated July 24, 1855.

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* This process of silvering glass was exhibited by Professor Faraday at the Royal Institution, at the Friday evening meeting, June 13.

THE CHEMICAL GAZETTE.

No. CCCXXXIII.—September 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Salts of Urea with Organic Acids. By H. HLASIWETZ.

OF the organic acids, only oxalic, cyanuric, lanthanuric, isocyanuric, uric, hippuric, and lactic acids have been examined as to their capability of combining with urea.

The statement that the last three form salts with urea has not been confirmed (Pelouze). The others however stand so nearly upon the boundary between organic and inorganic substances, and as cyanogen compounds are even so closely allied to urea, that it may be questioned whether this substance exhibits the same tendency to combine with other organic acids, or how far this goes as a general rule. To determine this, the author has made some experiments; and as he found that salts are very easily prepared with a number of crystallized acids, he thought that this property might be employed to establish the doubtful equivalents of some acids, which otherwise only give salts with difficulty. Thus the ease with which urea unites with gallic acid to form a very stable salt, led the author to hope that he might obtain similar salts with catechuic acid, cetraric acid, &c., as its weak basic nature excludes the rapid alterability which occurs with the salts of the inorganic bases, and which renders their preparation so difficult or entirely impossible. But these latter endeavours gave no result, and it is difficult to say what conditions must be fulfilled to obtain salts of urea. The compounds obtained are the following:—

a. *Acids of the formula* $C^n H^{(n-2)} O^8$.—Of this series only the oxalate of urea is hitherto known; but

Succinate of Urea, $C^8 H^4 O^6 + 2(C^2 H^4 N^2 O^2) + 2HO$, may be prepared with equal ease. A solution of 2 parts of urea and 1 part of succinic acid furnishes beautiful prismatic crystals with pointed ends. In dilute solutions they often become very large by long standing. They are not quite so difficult of solution in cold water as the oxalate; they have an acid reaction, taste of succinic acid, fuse when heated to 303° F., and evolve suffocating fumes. If these be allowed to pass into a flask, they condense therein into a fibrous crystalline mass, possessing the properties of succinimide. A hot solution of succinate of urea takes up large quantities of metallic oxides: thus magnesia and oxide of zinc are dissolved, and an evolution of ammonia is observed. When however a certain degree of saturation is attained, a crystalline precipitate of a basic succinate is thrown down. The filtered fluid then gives crystals of two kinds on evaporation, the one consisting of pure urea, and the other of the neutral succinate of the metallic oxide added. These double compounds, therefore, if any such exist, are very easily decomposable.

Succinate of urea is one of the neutral succinates. Analysis:—

C	30·55	12 =	72	30·25
H	6·26	14	14	5·88
N	23·20	4	56	23·52
O	..	12	96	40·35

Attempts to combine suberic and pimelic acids with urea were unsuccessful; the two substances crystallized separately.

b. *Acids of the Formula* $C^n H^n O^4$.—Urea does not combine with the acids of this numerous series. The volatile acids evaporate from a solution of urea, whether they are brought together directly or by the decomposition of their lime-salt and oxalate of urea; pure urea is left. The statement of Pelouze, in contradiction to a previous assertion, that there is no lactate of urea, also agrees with this, as it is probable that this behaviour will also occur with the derivatives of the series. The higher members of the series, the non-volatile fatty acids, do not combine with urea. The experiments were made with alcoholic solutions of the two substances.

c. *Acids*$=C^{n2} H^{(n2-8)} O^4$, *and their Allies*.—Experiments to combine benzoic, cinnamic, hippuric, and phenylic acids with urea gave no result. Their radicals, however, as also those of the series $C^n H^n O^4$, are capable of replacing the hydrogen in urea; relations which may perhaps be mutually exclusive. It is remarkable however that nitrophenisic acid gives no salt with urea, whilst the oxypicrate is very easily obtained. If nitrophenisic acid and urea be dissolved in equivalent proportions, the acid crystallizes from the solution very quickly, and the yellow mother-liquor furnishes urea. If the substances be dissolved in such proportions that the urea may be in excess, the solution does not crystallize for some time, but the crystals consist of urea, and the mother-liquor contains the acid, which at last crystallizes intermixed with the urea.

Oxypicrate of Urea$=C^{12}\begin{pmatrix} H^2 \\ 3NO^4 \end{pmatrix} O^3 + 2(C^2 H^4 N^2 O^2)$.—A hot solution of 2 parts of urea and 1 part of oxypicric acid furnishes on cooling very beautiful acicular or laminar crystals of this salt. They fuse readily, and do not explode with a strong heat; they furnish a white crystalline coat in the tube, and ammonia is evolved. At 212° F. they lose nothing in weight. Their composition agrees with that of the bibasic ammoniacal salt. The analysis gave—

C	..	..	16 =	96
H	..	..	10	10
N	27·52	27·07	7	98
O	..	..	19	152

d. *Tartaric Acid Group. Tartrate of Urea,* $2(C^8H^4O^{10})+C^2H^4N^2O+HO$.—A solution containing rather more than an equivalent proportion of urea crystallizes, when brought to the thickness of a syrup, forming prismatic crystals, which are generally very closely grouped. They are pressed dry between paper, then quickly washed with a little ice-cold water, and again pressed. They taste and react like free tartaric acid, are very soluble in water, fuse and become inflated, giving off an odour of ammonia and burnt sugar, and leaving a coal which is difficult of combustion. Analysis:—

C	..	..	18 =	108	32·43
H	..	..	13	13	3·94
N	8·21	8·19	2	28	8·40
O	..	..	23	184	55·27

Tartrate of Urea and Magnesia, $2(C^8H^4O^{10})+C^2H^4N^2O^2, MgO$, is a granular salt of a rather bitter taste, readily soluble and easy of fusion, when it evolves ammonia and leaves a coal, which is extremely difficult to reduce to ashes. The formula requires 6·08 per cent. MgO; found, 5·83 per cent.

Citrate of Urea, $C^{12}H^5O^{11}+C^2H^4N^2O^2+2HO$.—This was prepared in the same way as the preceding. It crystallizes more readily, and in large crystals of the form of citric acid. Its taste, reaction, and behaviour when heated, and towards metallic oxides, are the same as those of the tartrate. The zinc compound crystallizes in small grains; the magnesia-salt, after long standing, forms united prisms. Analysis:—

C	34·28	14 =	84	34·56
H	5·05	11	11	4·52
N	11·87	2	28	11·52
O	..	15	120	49·40

Meconate of Urea, $C^{14}HO^{11}+3(C^2H^4N^2O^2)+3HO$.—Prepared from 4 parts of urea and 1 part of meconic acid. It crystallizes rapidly from the cooled solution in prismatic scaly crystals. It is a tribasic salt of this acid. Analysis:—

C	31·55	20 =	120	31·57
H	4·64	16	16	4·21
N	..	6	84	22·10
O	..	20	160	42·12

No salts were obtained with kinic and aspartic acids.

e. *Uric Acid Series.*—To the already-known salts with acids of this series (cyanuric, isocyanuric, and lanthanuric acids) is added

Parabanate of Urea, $C^6H^2N^2O^6+C^2H^4N^2O^2$.—1 part of parabanic acid and 1½ part of urea, dissolved by boiling, gave concentrically-grouped flat prisms. They are difficult of solution in cold water, but dissolve in boiling alcohol. When heated in a tube, they fuse, the mass becomes brown, and a penetrating bitter odour is evolved, with formation of a crystalline sublimate. No evolution of ammonia is observed. Analysis:—

C	27·32	8 =	48	27·58
H	3·74	6	6	3·44
N	31·88	4	56	32·18
O	..	8	64	36·80

Alloxantine and Urea, $C^8 H^5 N^2 O^{10} + 2(C^2 H^4 N^2 O^2) + HO$.—1 part of alloxantine and 2 parts of urea were dissolved separately by the assistance of heat. The mixed fluids soon furnished small, flat, shining crystals. When the solution is heated, it becomes rose-coloured; the air-dried salt also becomes red at about 86° F., and it was therefore dried under the air-pump. When heated in a tube, the crystals decrepitate, and become purple, and afterwards brown, with evolution of hydrocyanic acid. When heated with alcohol, they become dull, but do not dissolve. The aqueous solution has an acid reaction. Towards baryta-water, muriate of ammonia, and nitrate of silver it behaves like pure alloxantine. Analysis gave:—

C	..	12 =	72	
H	..	14	14	
N	29·03	6	84	28·96
O	..	15	120	

Alloxane furnishes no compound when treated like alloxantine. (When the vapour of anhydrous hydrocyanic acid is passed over heated urea, no combination takes place, such as is entered into by muriatic acid under the same circumstances.)

f. *The so-called Lichen Acids.*—The author had no other representative of this series at hand, except the phloretic acid recently prepared and described by him, which, as he has shown, closely approaches beta-orsellic, evernic, and erythric acids.

Phloretate of Urea, $2(C^{18} H^{10} O^5) + C^2 H^4 N^2 O^2 + HO$, crystallizes in broad shining laminæ or in plumose crystals, which may be easily obtained from a solution of 3 parts of urea and 1 part of phloretic acid. Analysis:—

C	58·84	38 =	228	59·22
H	6·42	25	25	6·49
N	..	2	28	7·27
O	..	13	104	27·02

g. *Tannic Acids.*—Quercitannic and chinovatannic acids could not be combined with urea. Acids, such as those named, which are only capable of forming amorphous salts, are perhaps generally incapable of combining with urea.

Gallate of Urea, $C^{14} H^6 O^{10} + C^2 H^4 N^2 O^2$, is prepared much more readily and in finer condition than any described gallate. On the cooling of hot solutions of 2½ to 3 parts of urea and 1 part of gallic acid, it crystallises in large, and often very thick prisms, nearly an inch in length, belonging to the clinorhombic system, and separates so completely that the mother-liquor only retains a trace of it. It is an essential condition for its formation that the urea should be in excess. With 2 parts of urea and 1 part of acid, gallic acid crystallizes together with some salt. With a still smaller proportion of urea, crystals of gallic acid are first obtained, although the equivalent proportions according to the formula are 1 part of urea and 2·2 parts of gallic acid. It should be observed however that when the quantity of urea was not sufficient, so that at first only gallic acid crystallized, and this was left for several days in the solution, the globular tufts of gallic acid gradually disappeared again, and in their place well-formed crystals of the typical form of the clinorhombic system made their appearance, and increased in size until at last they were nearly as large as a pea. They are remarkable for their regularly developed form and the strong refractive power which they possess, especially whilst they are small. In their composition they are identical with the preceding crystals.

When gallate of urea is dissolved with a view to recrystallize it, the entire fluid soon sets into the voluminous fine crystals of gallic acid, and the salt is consequently never obtained again. Hence, even for mere recrystallization, some urea must be added to it. When this is done in the cold, the last-mentioned shining crystals of the salt again make their appearance.

Gallate of urea is very difficult of solution in cold water. It fuses, evolves ammonia, and then burns with flame. Perchloride of mercury produces a yellowish-red flocculent precipitate in its solution; in other respects it behaves with most reagents like pure gallic acid. Analysis:—

C	41·08	42·08	16	=	96	41·74
H	4·48	4·80	10		10	4·34
N	12·01	12·23	2		28	12·17
O	..	..	12		96	41·75

If catechuic acid, as has often been asserted, were analogous to gallic acid, it might be supposed that it would yield a similar compound, and this would have rendered it possible to determine its equivalent, upon which very various views are still entertained. But catechuic acid, prepared according to the method recently described by Neubauer, furnished no such salt either in an alcoholic or an aqueous solution; the acid crystallized first, and the urea remained in the mother-liquor. The author also attempted the formation of pyrogallate and cetrarate of urea with the same negative result.

All these acids, which in the presence of alkalies have such a tendency to take up oxygen and undergo a sort of humification, remain long unaltered in a solution of urea kept in lightly closed vessels, and then only become slightly brownish.

Taking into consideration the close agreement in chemical behaviour of pyrogallic, catechuic, and cetraric acids (and perhaps of chinone), it may be supposed that these four bodies are members of a series. As far as we know at present, they have in common the incapability of forming crystallizable salts, the instantaneous alteration by ammonia and the alkalies in the presence of air, and the power of reducing solutions of the readily deoxidized metals. The coloration of the solutions of iron-salts, and their behaviour towards chlorine, sulphuric acid, solutions of the alkaline earths, solution of gelatine, &c., are very similar. Their formulæ prove that they at least contain H and O in equal equivalents:—

$C^{12}H^{6}O^{6}$, pyrogallic acid.
$C^{18}H^{10}O^{10}$, catechuic acid (Laurent).
$C^{34}H^{15}O^{15}$, cetraric acid.
$C^{12}H^{4}O^{4}$, chinone.

Knop and Schnedermann gave the formula $C^{34}H^{16}O^{15}$ for cetraric acid, but the one above given agrees equally well with the results obtained:—

C	60·25	60·06	60·05	34	=60·05	C	34	=60·17
H	4·63	4·64	4·71	16	4·69	H	15	4·42
O	..	..	..	15	35·26	O	15	36·41

Sitzungsber. der Akad. der Wiss. zu Wien, March 1856.

On the Action of Chloride of Sulphur (SCl) *upon some Salts of Organic Acids. By* Prof. Heintz.

When chloride of sulphur is brought in contact with formiate of baryta, an evolution of gas is observed. This is pure carbonic oxide gas. At the same time hydrated formic acid, chloride of barium, and sulphate of baryta are formed, and sulphur separates, in accordance with the formula—

$$4(C^{2}HO^{3}+BaO),3ClS=2S,SO^{3}+BaO,3ClBa,4CO,2C^{2}HO^{3}+HO.$$

Upon this a method may be founded for obtaining the hydrate of formic acid. Thus if 3 equivs. of chloride of sulphur be mixed gradually with a mixture of 4 equivs. of a dry formiate and 4 equivs. of water, the distillation of the mixture at a temperature of 230° to 248° F. furnishes pure hydrated formic acid. Melsens's method for the preparation of hydrated acetic acid is not applicable to formic acid, because acid formiates cannot be prepared. Anhydrous acetate of soda, under the influence of chloride of sulphur, gives origin to anhydrous acetic acid, according to the formula—

$$4(C^{4}H^{3}O^{3}+NaO),3ClS=3ClNa,SO^{3}+NaO,2S,4C^{4}H^{3}O^{3}.$$

Nevertheless in this case subsidiary products are formed, especially some which contain sulphur; and these render it impossible to employ chloride of sulphur in the preparation of pure anhydrous acetic acid. If the dry acetate of soda be put slowly into the chloride of sulphur, a small quantity of a fluid which is not miscible with water is also formed; this is more volatile but heavier than water, but the author was unable to ascertain its nature from the small quantity of it which he obtained. He endeavoured to obtain anhydrous acetic acid by the dry distillation of protacetate of mercury at as low a temperature as possible. But to produce decomposition, a temperature of 482° to 572° F. is required; and hence by this means, instead of anhydrous acetic acid, a mixture of hydrated acetic acid with acetone and a substance containing more oxygen (which however is not formic acid) is formed.

By the action of chloride of sulphur upon anhydrous benzoate of soda, perchloride of benzoyle, chloride of sodium, sulphate of soda, and sulphur are first formed, in accordance with the formula—

$$2(C^{14}H^{5}O^{3}+NaO)+3ClS=2S,SO^{3}+NaO,ClNa,2\left(C^{14}H^{5}\left\{\begin{matrix}O^{2}\\Cl\end{matrix}\right.\right).$$

But if an excess of benzoate of soda be employed, and the mixture be heated to 302° F. until the odour of perchloride of benzoyle has disappeared, it contains anhydrous benzoic acid. This decomposition is expressible by the following formula:—

$$C^{14}H^{5}\left\{\begin{matrix}O^{2}\\Cl\end{matrix}\right.C^{14}H^{5}O^{3}+NaO=2C^{14}H^{5}O^{3},ClNa.$$

Anhydrous benzoic acid may be very easily obtained pure by this method. The author recommends the extraction of the mass with water containing a little carbonate of soda, washing it with water, and pressing. It is then melted on the water-bath, alcohol of the temperature of 122° F. is added to it, until it is completely dissolved with the exception of the sulphur present. It is then filtered, and the filtrate left standing in the cold, when the anhydrous benzoic acid crystallizes. By repeatedly mixing boiling water with the solution separated from the crystals and leaving it to cool, more of these crystals may be obtained perfectly pure. The crystals first procured contain some sulphur, from which they may be freed by fusion in the water-bath, and pouring them away from the crystals of sulphur, which easily sink to the bottom. If the substance still appears rather yellow, they may be again dissolved in the same way, a little freshly calcined animal charcoal, washed with acid, added to the warm solution, which is then filtered and crystallized.

In examining the residue which remains after the completion of distillation, especially in the action of chloride of sulphur upon acetate of soda, the author observed, that besides rhombic octohedral sulphur, fine long acicular crystals were produced from the hot alcoholic solution. He found however that these crystals also were sulphur, and that they could be produced by boiling sulphur freshly precipitated from liver of sulphur with alcohol, and filtering the solution whilst hot. Common flowers of sulphur and precipitated sulphur which had been kept for some time did not furnish these acicular crystals.—*Bericht der Akad. der Wiss. zu Berlin*, 1856, p. 263.

On the Shells of the Mollusca, the Byssus, and the Chitine Question.

By J. SCHLOSSBERGER.

The shells of the acephalous Mollusca consist of at least two layers of different structure, as has been shown especially by Carpenter and Bowerbank. Hitherto no notice has been taken of the distinction between the anatomically different parts in the chemical investigation of shells.

In the oyster-shell the naked eye immediately recognizes three essentially different parts, namely—

1. The inner, shining, semi-transparent stratum; the nacreous layer (*subnacreous substance* of Carpenter).

2. The hard brown scales which appear on the upper shell, as the coating of the margins of the numerous shell laminæ which lie over each other (*prismatic cellular substance* of Carpenter).

3. The opake, chalky, triturable mass, which is found under the nacreous layer, especially in the neighbourhood of the muscular impression. All these substances leave an organic skeleton after treatment with acids.

The mineral constituents of these three layers, according to the author's analyses, are—

1. *Nacreous layer.*—41·7 per cent. CO^2, representing 94·7 per cent. $CO^2 CaO$; 2.2 per cent. of organic matter (calculated from the loss by calcination); 3·1 per cent. of other salts (and loss), found by subtraction. 43·25 per cent. CO^2, representing 98·2 per cent. $CO^2 CaO$; 0·8 per cent. of organic matter; 0·8 per cent. of other salts.

2. *Brown scaly substance.*—39·2 per cent. CO^2, representing 89·09 per cent. $CO^2 CaO$; 6·27 per cent. of organic matter; 4·64 per cent. of other salts.

3. *Chalky layer.*—39·0 per cent. $CO^2 = 88{\cdot}59$ per cent. $CO^2 CaO$; 4·70 per cent. of organic matter; 6·71 per cent. of other salts.

From this it appears that the nacreous layer is richest in mineral bodies, whilst the substances 2 and 3, notwithstanding their different structure and colour, agree in the quantity of $CO^2 CaO$, but not of the organic matter. The author also remarks, that phosphoric acid and alkali can be detected in bivalve shells in general when a sufficient quantity is employed for analysis. The examination of a series of other shells gave the following results:—

	CO^2. per cent.	CO^2CaO. per cent.
Venus decussata	41·14	93·51
Operculum of Turbo rugosa	42·48	96·55
Mytilus edulis (Young)	36·12	82·12
Bulimus radiatus	41·10	93·41
Voluta rustica	40·45	92·01
Cypræa erosa	41·45	94·21
—— chinensis	41·86	95·16
—— moneta	40·85	92·85
Oliva —— ?.............	41·00	93·20
Turbo neritoides	40·69	92·48
Turritella fuscata..........	39·02	88·70
Pupa (West Indies)........	41·10	93·48
Anodonta anatina..........	39·15	88·99
Helix nemoralis	36·34	82·62

The organic matter of the shells.—In the residue which remained undissolved after the treatment of oyster-shells with dilute acids the author found at least two different substances.

1. *Brown, tough, somewhat translucent membranes*, the largest of which were perhaps one-fourth the size of the shell itself, accompanied by numerous smaller ones.—After washing and drying, they were grayish-yellow, tolerably coherent, and nearly opake. Under the microscope they resembled the so-called calcareous vesicular layer (*Kalksackchenschicht*) of the Naiades, as described by Dr. Kost. The surface showed a brownish structureless substance, in which there were innumerable, mostly regular, rhombic, colourless spots. They were insoluble in water, even by long treatment with superheated water, and also in alcohol, æther, cold and boiling acetic acid, and diluted mineral acids. In cold sulphuric acid they swelled up a little, and became soft and transparent; their microscopic corpuscles became less distinct, but remained perceptible even after long contact with the acid; sometimes semi-lunar dark bodies (clefts?) made their appearance in them. When the sulphuric acid was heated, the whole dissolved with a yellow colour, but without evolution of sulphurous acid; the fluid only became brown by long heating. At last it became black. The solution in sulphuric acid, when neutralized by ammonia, gave an abundant precipitate with tannic acid. Strong boiling muriatic acid dissolved them with a brown colour, without any appearance of blue. Cold nitric acid left them unaltered; when heated, they became of a beautiful pure yellow, gradually crumbled to pieces, and dissolved without swelling. Even in the last portions remaining before solution, the microscope showed the rhombic corpuscles.

The brown membranes remained apparently unchanged after maceration for four weeks in cold solution of potash of 50 per cent., and also after boiling in the same fluid. The fluid acquired a deep yellowish-brown colour. By boiling with potash, they lost about 46 per cent., or nearly half their weight, which quantity was therefore dissolved. The undissolved portion evolved ammonia when fused with hydrate of potash. This substance was found to contain 16·7 per cent. of nitrogen by combustion with potash-lime. The ash effervesced strongly with acids, and contained no sulphur.

2. *White or grayish flakes*, which are partly slimy to the touch, and also represent membranes.—These do not possess the structure of the preceding, but are either homogeneous and folded, or indistinctly fibrous (or streaked). They possess much less firmness and no pigment, and belong partly to the nacreous layer, and partly to the chalky intermediate substance.

The foundation of the shells of the Mollusca is consequently certainly not chitine, as Kost has asserted. The analytical results do not differ greatly from Fremy's conchioline.

The portion of the brown scales dissolved in potash could not be prepared pure. Acids did not precipitate it from its solution. This portion is no proteine substance, but a peculiar body. The author found it again in the byssus. Amongst known substances, the mother-vesicles of *Echinococcus* appear to be of a very similar nature, and perhaps they are identical with the organic matter of the nacreous layer and chalky substance, which the author could not further investigate.

Byssus.—Lavini and Scharling have referred the byssus to the horny tissues; Leuckart has considered it as chitine, from its insolubility in potash. The author investigated the byssus of *Pinna nobilis.* He confirms Leuckart's statement, that the threads of byssus are insoluble in potash, at least when they are dry before treatment with potash. Byssus, extracted with water, alcohol, and æther, contained 13·5 and 13·9 per cent. of nitrogen. After extraction with potash and sufficient purification from the alkali, it gave on analysis only 12·2 and 12·6 per cent. of nitrogen. Byssus boiled with potash stands, as regards its amount of nitrogen, between Fremy's conchioline (with 16·5 per cent. of nitrogen) and the chitine of the Crustacea (6·5 per cent. nitrogen according to Schmidt).

Chitine.—The author ascertained that the portion of the shells and byssus which is insoluble in potash is not the same chitine that occurs in the skin of the Arthropoda; and it appears from his observations, that a number of different substances are included under the common name of chitine. He particularly brings forward Fremy's statement, that the chitine of the Crustacea and other Invertebrata is destitute of nitrogen, as the results of the investigations of Lassaigne, Payen, Children, Daniell, Schmidt, and himself are in direct opposition to it.—Liebig's *Annalen*, xcviii. p. 99.

On the Preparation of Benzamic Acid. By H. LIMPRICHT.

The action of protacetate of iron upon nitro-compounds appears always to be analogous with that of sulphuret of ammonium. Nitrobenzoic æthylic æther, when heated with metallic iron and acetic acid, becomes converted into benzamic æthylic æther. The acid separated from the latter by alcoholic solution of potash was converted into the baryta-salt, and the amount of baryta in this was determined. Two experiments gave 37·3 and 37·4 per cent. of barium.—Liebig's *Annalen*, July 1856, p. 118.

On the Origin of Nitre. By M. DESMAREST.

The author states that from the facts observed by him it results—

1. That the nitrogen and oxygen of the air are not capable of combining under the influence of electricity to form nitric acid.

2. That this acid is not formed under the influence of ozone when aërated water is decomposed by electricity.

3. That it is not formed by the oxidation of the nitrogen of ammoniacal gas or of organic matters, at the expense of the oxygen of the air.

4. That it is not formed when nitrogen is in the presence of an excess of oxygen, that is to say, in a case which does not usually occur in nature.—*Comptes Rendus*, July 14, 1856, p. 89.

On Phaseomannite, a new kind of Sugar, contained in the unripe Fruit of the Kidney Bean (Phaseolus vulgaris). By H. Vohl.

The author observed that the juice of the unripe fruit of the kidney bean possessed a very sweet taste, and that after complete fermentation and the distillation of the alcohol formed, the residue had lost none of its sweetness. He attributed this to the presence of mannite.

To prepare mannite from the beans, these were finely cut up, put into a press-bag, exposed for half an hour to hot steam or plunged into boiling water, and then strongly pressed. The brown fluid was mixed with yeast, fermented, and after fermentation neutralized with chalk or carbonate of soda. The fermenting fluid presented the odour of preserved beans.

The fluid produced was evaporated on the water-bath to the consistence of a syrup, and the extract-like mass exhausted with alcohol of specific gravity 0·863. The alcohol was distilled off, and the residue somewhat reduced in the water-bath, and left for twenty-four hours, when a quantity of flat needles, concentrically grouped, which might be taken for mannite, crystallized from it.

The crystals were freed from the mother-liquor, pressed between bibulous paper, and dissolved in weak alcohol. A small quantity of gum and vegetable gelatine separated, and were got rid of by filtration. When the alcohol had been distilled off, and the aqueous solution decolorized by animal charcoal, it furnished, by spontaneous evaporation, beautiful limpid prisms, partly grouped concentrically, very different in their external appearance from mannite. This body, which possesses a sweet taste, is readily soluble in water and dilute alcohol, but difficult of solution or insoluble in absolute alcohol and æther.

It loses water of crystallization in dry air, becomes dull, and more difficult of solution in water, from which however it separates on spontaneous evaporation with its original amount of water. At 212° F. it loses 16·5 per cent. of water.

When heated, the crystals decrepitate and give off water; between 302° and 320° F. they fuse to a colourless liquid, which solidifies in a crystalline form on cooling; when heated to 454°–472° F., the body begins to boil, with evolution of empyreumatic vapours, which diffuse an odour of burnt sugar. The vapour burns with a luminous flame, without smoking. The carbonaceous residue burns upon platinum without leaving an ash. When mixed with soda-lime and heated, the substance evolves no ammonia.

With a solution of sulphate of copper and potash, it gives a dark azure-blue solution, which does not deposit protoxide of copper either in the cold or by boiling.

The behaviour of this body with sulphate of copper and potash, and its incapability of fermentation, place it in the same series with mannite; but its behaviour in dry air and its composition give sufficient cause to distinguish it strictly therefrom. The author therefore calls it *phaseomannite.*

The combustion of the body, dried at 212° F. with chromate of lead, gave on the average of three analyses—

C	41·0475
H	6·8649
O	52·0876

From this the formula of the body dried at 212° F. is calculated as $C^{21} H^{21} O^{20}$. This formula requires—

C	41·042
H	6·840
O	52·118

Phaseomannite dissolves in cold concentrated sulphuric acid without blackening. The solution only becomes brown when heated to 212° F., deposits carbon, and evolves sulphurous acid. In cold concentrated nitric acid it dissolves without acquisition of colour or evolution of gas; on the addition of English sulphuric acid, a body separates in white flakes. In all probability this is the nitro-compound of phaseomannite.

Boiled with dilute sulphuric acid, it appears to undergo no alteration, and afterwards produces no protoxide of copper on the addition of sulphate of copper and potash. When heated with nitric acid, it forms oxalic acid.

Phaseomannite has a pretty strong purging action, which explains the production of looseness in the bowels by the use of beans.

The author observed that the beans contained this body in the greatest abundance when the seeds were still small, and that the phaseomannite disappeared as starch was formed.—Liebig's *Annalen*, July 1856, p. 125.

On Æthylonaphthylamine. By H. LIMPRICHT.

When bromide of æthyle and naphthylamine are heated together in an apparatus in which the condensed vapours of bromide of æthyle must flow back, or the two substances are left in contact for several days at the ordinary temperature, reddish warty crystals of hydrobromate of æthylonaphthylamine are formed, which are obtained colourless by repeated recrystallization. After drying over sulphuric acid, they gave 31·5 to 31·7 per cent. of bromine; the formula $C^{20} H^{8} (C^{4} H^{5}) N, HBr$ requires 31·7 per cent. of bromine.

Potash separates naphthylamine, and not æthylonaphthylamine, from the solution of this salt, so that it was impossible to study the properties of the pure substance, and especially its behaviour towards bromide of æthyle. Its decomposition with potash is explained by the following equation:—

$$C^{20} H^{8} (C^{4} H^{5}) N, HBr + KHO^{2} = C^{20} H^{9} N + C^{4} H^{6} O^{2} + KBr.$$

Hydrobromate of æthylo-naphthylamine. Naphthylamine. Alcohol.

Liebig's *Annalen*, July 1856, p. 117.

On the Superphosphate of decomposed Bones. By W. Wicke.

Starting from the supposition that the acid phosphate of lime in the bones is very soon converted into neutral phosphate in the soil, the opinion has been set up that the superphosphate only acts by its fine state of division. It has even been recommended to precipitate again the acid phosphate of lime rendered soluble by sulphuric acid by means of lime, and to incorporate this with the soil.

As far as I am aware, no experiments have been made upon the behaviour of the superphosphate towards the ordinary constituents of the soil, which may have a neutralizing action upon it; I mean towards carbonate of ammonia, as the ordinary product of decomposition of the organic constituents of urine and carbonate of lime. Both these bodies certainly have a decomposing action upon the superphosphate, but not of such a nature as to separate the whole of the phosphoric acid in an insoluble compound. In the former case a sufficient quantity of phosphate of ammonia for the requirements of the plants, and in the second an acid salt, remains in solution.

For this experiment I employed very pure marl. If the superphosphate be filtered through the marl, or left in contact with it for a long time, a portion of the phosphoric acid is certainly combined with evolution of carbonic acid, but the salt is not entirely precipitated. Even in this case we present immediately to the plant a phosphate which is soluble in water.

The soluble salts of iron have an injurious action upon decomposed bones as a manure. A loss must take place. A solution of sulphate of iron immediately produces a white precipitate with an aqueous solution of superphosphate, and this perceptibly increases, so that the greater part of the phosphoric acid is soon separated as an insoluble iron-salt.

Bones decomposed with sulphuric acid are extracted with water at a gentle heat. The yellowish filtrate has a strongly acid reaction.

15 cub. centims. of solution contained 0·0103, or 0·0686 per cent. of sulphuric acid, and 0·0225 or 0·15 per cent. of lime, leaving 0·0153 of lime for the phosphoric acid.

15 cub. centims. of the solution contained 0·1047, or 0·698 per cent. of phosphoric acid. The equivalent proportion of the lime to the phosphoric acid is therefore as 1 to 8.

15 cub. centims. of the solution were mixed with carbonate of ammonia until the production of a weak alkaline reaction. A strong white precipitate was produced, which gave on analysis 0·043, or 0·286 per cent. of lime, and 0·0313, or 0·2086 per cent. of phosphoric acid. Proportion of lime to phosphoric acid as 3 to 1.

The filtrate still contained 0·0706, or 0·4706 per cent. of phosphoric acid. The whole quantity of phosphoric acid was 0·1047
Obtained .... 0·1019
Loss .... 0·0028

Experiment with Marl.—The superphosphate remained for several days in contact with the marl. It was then filtered, and the fluid brought to its original quantity (15 cub. centims.). The filtrate had an acid reaction. It contained 0·011, or 0·073 per cent. of lime, and 0·0578, or 0·3853 per cent. of phosphoric acid.

From these experiments it appears that it is not advisable to convert the superphosphate again into tribasic phosphate of lime by the addition of lime. By the action of ammonia upon the acid product, the desired state of fine division is at once produced, whilst another portion of the phosphoric acid can be drawn up by the plants in the form of phosphate of ammonia at the commencement of vegetation. This is also the case when carbonate of lime acts upon the superphosphate.—Liebig's *Annalen*, July 1856, p. 97.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Note on the Precipitation of various Salts from their Solutions.

By F. MARGUERITTE.

WHEN muriatic acid is mixed with a solution of chloride of sodium, the latter is immediately, if not completely precipitated. But if a current of muriatic acid gas is passed until rejection into a solution of common salt, the latter is precipitated within a few thousandths and the liquid muriatic acid left in the fluid is in such a state of purity that it may be sold.

With a mixed solution of the chlorides of sodium and potassium, the chloride of sodium is first precipitated, so that by dividing the operation the separation of these two salts may be effected in a certain degree. The insolubility of the chlorides of sodium and potassium in muriatic acid is so great, that under its influence the sulphates of soda and potash are decomposed into insoluble chlorides, and free sulphuric acid eliminated in the liquid. This decomposition may go very far; thus muriatic acid gas, when passed until rejection into a solution of sulphate of potash, converts nearly 70 per cent. of the latter into chloride of potassium, setting free a corresponding amount of sulphuric acid.

The double sulphate of potash and magnesia undergoes a similar decomposition. Sulphate of magnesia does not participate in this reaction, and, like the chloride of magnesium, it is not precipitated by muriatic acid unless under particular conditions of concentration.

Sulphate of soda, under the same circumstances, is decomposed in a more complete manner, in consequence of the greater insolubility of chloride of sodium in muriatic acid. The precipitation of the chlorides of sodium and potassium in this way appears capable of industrial application—

1. In the preparation of a quality of salt for special purposes;
2. In the production of crude salt; and

3. In the separation of chloride of potassium from the mother-liquors of salt marshes.

The peculiar state of the salt precipitated by muriatic acid, its extreme division, its whiteness and brilliancy, its perfect purity, and the simplicity of its preparation, render it preferable for the purposes of luxury to every kind of salt, whether obtained by trituration or by evaporation with heat. It is obtained perfectly pure by operating upon common salt-water, and still better with a solution of common salt. The acid liquid is decanted, and the precipitate dried upon the sole of a furnace heated in a suitable manner, by which the salt is purified from the muriatic acid with which it is impregnated. Before drying the precipitate, it may be washed with the salt solution, which is afterwards to be submitted to precipitation. This washing removes nearly the whole of the muriatic acid. Lastly, the excess of acid may be saturated with carbonate of soda, the cost of which would not be greater than that of heating the drying furnace, and this would allow it to be spread out, and dried in the open air.

The passage of the gas keeping the liquid in a state of continual agitation causes the precipitation of the salt in extremely fine grains; but it may be obtained in large crystals when the muriatic acid is allowed to dissolve at the surface of a liquid in repose, as is usually done in the condensation of this acid.

The separation of chloride of potassium from the mother-liquors of salt marshes is more rapid, more complete, and cheaper than the process now employed, which consists in concentrating the mother-liquors by heat, and leaving them to crystallize under conditions of temperature which are not always to be obtained with certainty. Moreover, the product obtained is a triple chloride of sodium, potassium, and magnesium, a compound which must be purified by successive crystallizations, causing a loss of time, fuel, and material. By the action of muriatic acid upon the mother-liquors, nearly the whole of the chlorides of sodium and potassium contained in them is obtained; the chloride of magnesium remains in the solution, which may be employed in the manufacture of chloride of lime. The chlorides of sodium and potassium are separated without difficulty, either by dividing the precipitation, or by their different degrees of solubility when hot and cold.

The advantages of this process in the production of crude salt do not appear to be doubtful. About salt-works there are generally manufactories of sulphate of soda, which are a constant source of muriatic acid. The whole of this acid is not collected in some places, its sale being difficult from the cost of transport. Supposing that all the muriatic acid produced would be sold, 100 kilogrms. of salt converted into sulphate of soda would reproduce rather more than 33 per cent. of their weight in common salt. If it were found more advantageous to apply all the muriatic acid in precipitation, a much larger quantity of salt would be regenerated in this manner. 100 kilogrms. of chloride of sodium, decomposed by sulphuric acid, give 62.39 kilogrms. of muriatic acid, which require 109·1 kilogrms.

of water to furnish a solution of the density of the muriatic acid of commerce (1·18). This quantity of water at the ordinary temperature would dissolve, and consequently allow of the precipitation of 38·18 kilogrms. of salt.

The solution of muriatic acid, if it be not sold, will give when gently heated 43·2 kilogrms. of gas, which precipitate 26·45 kilogrms. more salt; and the solution, when deprived of all the gas which it is capable of giving off, will represent acid with 16 equivs. of water, which is still serviceable for some purposes. In these two operations the quantity of salt precipitated will be 64·65 kilogrms. This is theoretical; but if we consider the quantity of salt reproduced as 50 per cent. only, this valuation will not appear exaggerated when we consider the efficacy of the means and the simplicity of the operation.

The principle of this operation consists in the employment of a volatile agent, which, after serving to precipitate the salt, may be driven off by heat, without leaving any impurity behind it. Upon the same principle several other salts may be eliminated from their solutions, although in a less complete manner. Carbonate of soda may be precipitated in a state of great purity by ammonia from a solution of common soda; the crystalline salt obtained, when dried upon a stove, does not retain the smallest trace of ammonia. Moreover, the same quantity of ammonia will serve almost for an indefinite period, as it is sufficient to heat the ammoniacal liquid to recover all the gas which it had dissolved. Ferrocyanide of potassium, and some other salts, are also precipitated by ammonia.—*Comptes Rendus*, July 7, 1856, p. 50.

Artificial Meerschaum. *By* L. Wagenmann.

If carbonate of magnesia be mixed with an eighth of its weight of calcined magnesia, and a little paste of lime obtained from calcined marble and solution of soluble glass be added to it, the mass, after complete drying, is not unlike meerschaum, and may find employment in the arts. The alkaline salt produced is extracted by water from the dry meerschaum, which is then boiled with wax.—*Journ. für Prakt. Chem.*, lxvii. p. 502.

New Mode of Manufacturing Malleable Iron and Steel without Fuel. *By* Mr. H. Bessemer*.

The essential feature of Mr. Bessemer's invention is, that he takes crude iron directly from the ordinary blast-furnace, and in the incredibly short space of thirty minutes converts it into ingots of malleable iron or steel of any size, and fit for the various manipulations ordinarily employed to adapt them to all the material purposes to which they are now applied. He thus dispenses with all the intermediate processes to which recourse has been had to produce the same effect within the last seventy years, including the making iron into pigs, and the refining, puddling and squeezing stages, with all their attendant labour and fuel. Paradoxical as it may seem, it is not the less true, that he has achieved this great result by the application to the iron, in its transition from the blast-furnace to the condition of the ingot, of a heat inconceivably intense, generated without furnace or fuel, and simply by blasts of cold air. By this means he not only avoids the injurious action of mineral fuel on the iron under operation, which has always deteriorated the quality of English iron, but saves all the expense of the fuel. He sets out with the assumption that crude iron contains about 5 per cent. of carbon; that carbon cannot exist at a white heat in the presence of oxygen without uniting therewith and producing combustion; that such combustion would proceed with a rapidity dependent on the amount of surface of carbon exposed; and, lastly, that the temperature which the metal would acquire would be also dependent on the rapidity with which the oxygen and carbon were made to combine, and consequently that it was only necessary to bring the oxygen and carbon together in such a manner that a vast surface should be exposed to their mutual action, in order to produce a temperature hitherto unattainable in our largest furnaces. With a view of testing practically this theory, he has constructed a cylindrical vessel of 3 feet in diameter and 5 feet in height, somewhat like an ordinary cupola-furnace, the interior of which is lined with fire-bricks, and at about 2 inches from the bottom of it he inserted five tuyère pipes, the nozzles of which are formed of well-burnt fire-clay, the orifice of each tuyère being about three-eighths of an inch in diameter. At one side of the vessel, about half-way up from the bottom, there is a hole made for running in the crude metal, and on the opposite side there is a tap-hole stopped with loam, by which the iron is run out at the end of the process. The vessel is placed so near to the discharge-hole of the blast-furnace as to allow the iron to flow along a gutter into it, and a small blast-cylinder is used capable of compressing air to about 8 lbs. or 10 lbs. to the square inch. A communication having being made between it and the tuyères, the converting vessel is in a condition to commence work. The blast being turned on, and the fluid iron run into the vessel, a rapid boiling up of the metal is heard going on within the vessel, the metal being tossed violently about and dashed from side to side, shaking the vessel by the force with which it moves, from the throat of the converting vessel. This continues for about fifteen or twenty minutes, during which the oxygen in the atmospheric air combines with the carbon contained in the iron, producing carbonic acid gas, and at the same time evolving a powerful heat. The rapid union of carbon and oxygen adds still further to the temperature of the metal, while the diminished quantity of carbon present allows a part of the oxygen to combine with the iron, which undergoes combustion and is converted into oxide. At the excessive temperature that the metal has now acquired, the oxide, as soon as formed, undergoes fusion, and forms a powerful solvent of those earthy bases that are associated with the iron. The violent ebullition going on mixes most intimately the scoria and metal, every part of which is thus brought in contact with the fluid oxide, which washes and cleanses the metal most thoroughly from the silica and other earthy bases that are combined with the crude iron, while the sulphur and other volatile matters which cling so tenaciously to iron at ordinary temperatures, are driven off, the sulphur combining with the oxygen and forming sulphurous acid gas.

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* Abstract of a paper read at the recent Meeting of the British Association at Cheltenham;—the paper will be found at length in the Supplement to the Mining Journal for August 16th, 1856.

At that stage of the process immediately following the boil, the whole of the crude iron has passed into the condition of cast steel of ordinary quality. By the continuation of the process, the steel so produced gradually loses its small remaining portion of carbon, and passes successively from hard to soft steel, and from soft steel to steely iron, and eventually to very soft iron; hence, at a certain period of the process, any quality of metal may be obtained. There is one in particular, which, by way of distinction, may be called semi-steel, being in hardness about midway between ordinary cast steel and soft malleable iron. This metal possesses the advantage of much greater tensile strength than soft iron. It is also more elastic, and does not readily take a permanent set, while it is much harder, and is not worn or indented so easily as soft iron. At the same time, it is not so brittle or hard to work as ordinary cast steel. These qualities render it eminently well adapted to purposes where lightness and strength are specially required, or where there is much wear, as in the case of railway cars, which from their softness of texture soon become destroyed. The cost of semi-steel will be a fraction less than iron, because the loss of metal that takes place by oxidation in the converting vessel is about 2½ per cent. less than it is with iron; but as it is a little more difficult to roll, its cost per ton may be fairly considered to be the same as iron. But as its tensile strength is some 30 or 40 per cent. greater than bar iron, it follows that for most purposes a much less weight of metal may be used; so that, taken in that way, the semi-steel will form a much cheaper metal than any that we are at present acquainted with.

On the Preparation of Aluminium. By C. BRUNNER.

The author describes a process for the preparation of aluminium from fluoride of aluminium, which, as has been shown by H. Rose, may be better adapted for furnishing this metal than the chloride. The peculiarity of the following process consists in the production of a cheap fluoride of aluminium, by which cryolite is rendered unnecessary.

Alum, freed as far as possible from iron by frequent recrystallization, is converted into burnt alum in the usual way. In this operation the salt is heated until vapours of sulphuric acid are recognizable. The mass is then reduced to a coarse powder, and this is exposed for about two hours to a strong red heat in a crucible. On cooling, the caked mass is triturated, and nearly washed out with water. The substance thus obtained is alumina, which still retains a small quantity of sulphuric acid (no doubt in the form of basic salt), which cannot be got rid of by washing. The imperfectly washed mass is then dried until it can be detached from the filter, and stirred with a concentrated solution of carbonate of soda. For this purpose only a small quantity of this salt is required, not more than one-tenth of the alum operated upon. The pasty mixture is then dried, and the residue moderately calcined for about an hour. By this operation the acid is entirely extracted from the basic sulphate of alumina. If the mass be extracted by boiling with water, the residue is pure alumina, which may easily be washed.

If, in the above operation, a larger quantity of carbonate of soda is employed than that directed, a portion of the alumina combines with it, dissolves during the washing, and is thus lost. In the above proportions this loss is very inconsiderable.

To convert the alumina into fluoride of aluminium, it is exposed at a high temperature to fumes of hydrofluoric acid. For this purpose, when the experiments are made with small quantities (such as 8 grms.), the alumina is put into a platinum crucible, which is hung obliquely by means of an iron wire over a good spirit-lamp or a charcoal-fire, and heated until the commencement of redness. The fumes of hydrofluoric acid, which are evolved from a leaden or platinum retort, are then allowed to penetrate into the midst of the alumina, which is frequently stirred with a platinum spatula, in order to bring all parts of it into contact with the gas.

As the powdered alumina does not perceptibly change in appearance in this operation, the increase in the weight of the substance must be observed from time to time, in order to ascertain the progress and completion of the operation.

Calculation shows that if alumina, $Al^4 O^3$, is to be converted into $Al^4 F^6$ (and this compound appears to be formed), 100 parts must become 163·9. This point can only be attained by long operation, the cause of which may be, that the fluoride of aluminium produced encloses the remainder of the alumina, and thus renders the complete conversion more difficult. This circumstance however is of no essential disadvantage subsequently. Time and trouble may be saved when the increase is only continued to 150. It is essential to get the proper degree of heat in this operation, as the compound is produced with far more difficulty at higher and lower temperatures. The most favourable temperature appears to be just as redness is commencing. Frequent stirring is also advisable, and this may be constant with large quantities.

In the employment of 8 grms. of alumina, this operation usually required an hour and a half. It is clear however that with a proper arrangement of the apparatus many pounds might be prepared in the same time. The compound thus obtained occupies nearly double the space of the original calcined alumina, and this increase of volume occurs principally towards the end of the operation. The substance should be kept in bottles.

For the reduction of the metal, the author adopted the method recommended by Rose and Deville. The fluoride of aluminium, prepared as above, is put into a Hessian crucible with half its weight of sodium cut into thin plates, the fluoride and the sodium being placed in alternate layers. The whole is then pressed with a stamp as tightly as possible into the crucible, and covered about half an inch deep with fused chloride of sodium broken into small pieces. The crucible is furnished with a cover, or what is better, with a round fire-proof brick.

When thus arranged, the whole is exposed to pretty strong heat, for which purpose a small Sefström's furnace with a blast is the best. It is essential that a good red heat, but not a white heat, should be attained, as otherwise the reduced metal is not properly fused; but it must also be borne in mind that the heat must not be maintained too long after the completion of the reduction, as in this case a portion of the reduced metal may be burnt away, or the crucible may be injured by the action of the fluoride of sodium. A hissing or crackling is usually heard in the crucible at the moment of reduction. From this time the heat should only be continued about five to eight minutes, and the fused mass should be stirred with a clay-pipe stem, so that the aluminium may run together to a single lump; the fire is then immediately put out by covering it up and closing all the openings of the furnace, and the apparatus is left to cool.

When quite cold, the crucible is put into a vessel of water, by which the gray saline mass is softened. This is then removed, and at the bottom of the crucible the reduced aluminium is found in the form of a round, perfectly metallic ball. The saline mass still contains a considerable portion of finely divided metal, partly in small grains, and partly in a grayish, somewhat coarse powder, which, when rubbed in an agate mortar, acquires a metallic lustre. This is collected and purified by lixiviation, during which tolerably large fused globules sometimes make their appearance. In this operation a hydrogen gas of disagreeable odour is usually evolved. It is advisable to renew the water very frequently, as the alkaline solution formed has an oxidizing action upon aluminium.

When the roundish metallic bodies are collected by this operation, it is unnecessary to treat the residuary amorphous powder for the purpose of obtaining aluminium; at least the author never succeeded in fusing it into a mass. On the other hand, this residue frequently contains a considerable portion of silicium, doubtless produced from the crucible. This is the same product that was observed by Deville, and recently described by Wöhler. Sometimes single silicium grains may be isolated, by treating the finely divided aluminium with muriatic acid.—*Berner Mittheilungen*, May 1856; and Dingler's *Polyt. Journal*, cxl. p. 357.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Water upon Glass. By J. Pelouze.

The author refers to the observations of Scheele, Lavoisier, Chevreul, and other chemists, upon the action of water upon glass, but remarks that no one has yet attempted to determine the extent of the alteration thus produced. The action of water upon glass reduced to powder is the principal object of his memoir.

The action of boiling water is excessively slow upon glass vessels in which it is boiled, and when cold it has still less action, but it decomposes powdered glass with extraordinary ease. Thus a bottle of half a litre scarcely loses 1 decigrm. when water is boiled in it for five whole days; but if the neck be cut off and powdered and boiled in the same vessel for the same time, it loses nearly a third of its weight. The same vessel which has contained water for years without losing appreciably in weight, will lose 2 or 3 per cent. in a few minutes by simple contact with cold water when pulverized. The following are the results of some of the author's experiments:—

1. A specimen of white glass, of the best commercial quality, consisting of—

Silica	72·1
Soda	12·4
Lime	15·5
Alumina and oxide of iron	traces

was very finely powdered on a plate of agate; 5·510 grms. were boiled in a porcelain capsule with frequently renewed distilled water. The clear liquids were evaporated and the residue calcined; it weighed 0·175.

The portion insoluble in water was treated with water acidulated with muriatic acid, when a pretty brisk effervescence was observed. The muriatic acid solution was saturated with ammonia, which produced a slight precipitate (alumina), an excess of oxalic acid was added, the oxalate of lime was collected, washed, dried, and decomposed by sulphuric acid; it gave 0·190 of sulphate of lime, representing 0·078 of lime, or 1·5 per cent. of the weight of glass employed. The glass containing 15 per cent. of lime, we may conclude that the water had decomposed about 10 per cent. of the glass.

2. Another white glass, also of the finest quality, composed of—

Silica	77·3
Soda	16·3
Lime	6·4
Alumina and oxide of iron	traces

5·180 grms. of glass were operated upon in precisely the same way as the last. The residue of the aqueous solution was 0·945 grm.; the weight of the sulphate of lime, 0·250, representing 0·103 of lime, or 2 per cent. of the weight of glass. The glass containing 6·4 per cent. of lime, 32 per cent. of the glass must have been destroyed. The residue of the aqueous solution contained 0·281 grm. of soda, or 5·6 per cent. of the weight of the glass; the remainder was silica. The glass containing 16·3 per cent. of soda, 34 per cent. of glass had been attacked.

The composition of the silicate of soda dissolved in the water was $3(SiO^3)2NaO$; at 302° F. it retained 2 equivs. of water.

3. The two kinds of glass just mentioned were agitated for a few minutes with cold water, a few drops of weak muriatic acid were added to the mixture, which was filtered immediately. The loss of weight of the glass and the amount of lime collected showed that the glass had lost 2 to 3 per cent. by this simple contact with cold water.

By boiling for a few minutes, the same glass lost nearly double, or between 5 and 6 per cent.

4. All sorts of commercial glass, when finely powdered and exposed to the air, are slowly decomposed, absorb carbonic acid by degrees, and after some time effervesce briskly with acids. The same effervescence takes place with acids in a mixture of powdered glass and water which has been left in the air for a few days. The acid water contains a large quantity of soda and lime.

Sulphuric acid also is almost always found; as most glasses contain sulphate of soda, varying in weight from one- or two-thousandths to two-hundredths.

5. Finely-powdered glass, boiled with water into which a current of carbonic acid is passed, absorbs this gas in a few moments, and afterwards effervesces briskly with acids.

6. Powdered glass, boiled for several hours with sulphate of lime, produces a considerable quantity of sulphate of soda. This reaction explains why the walls and the floors of workshops, in which plate-glass is polished, are always covered with an efflorescence of sulphate of soda. The plaster which serves to fix the glass furnishes the sulphuric acid, and the glass the soda, of which this salt is composed.

7. All glasses reduced to fine powder immediately restore the blue colour of red litmus-paper and tincture, and change syrup of violets to green. Powdered glass which has undergone the action of cold water, continues to alter in boiling water.

8. Crystal-glass in fine powder, agitated for a few minutes with water containing a very small quantity of acid, gives a black deposit of sulphuret of lead by treatment with sulphuretted hydrogen.

After half an hour's ebullition with water and the addition of an acid, 5 grms. of crystal in powder furnished 0·050 of sulphuret of lead, representing a decomposition of about 3 per cent. Flint-glass, which contains still more oxide of lead, undergoes a still more considerable decomposition.

Devitrified glass behaves like ordinary glass with water, except that it appears to be still more easily decomposed.

After boiling for five days, a specimen of glass similar in composition to the first-mentioned had undergone a decomposition corresponding to a third of its weight, and the silicate of soda yielded by it had also the formula—

$$3(SiO^3)\,2NaO.$$

Thus powdered glass is decomposed by contact with water or air with an ease and rapidity which appear very extraordinary, considering the great stability of vessels formed of cast or blown glass. Is the surface of the glass in this form in a particular state, which modifies its properties? This does not appear probable when we consider that plate-glass, from the surface of which several millimetres have been removed in polishing, is equally, if not more permanent in moist air and water than common glass, and that in all cases the crude plate-glass presents neither more nor less resistance to atmospheric agents than the others The author regards the difference in the action of water upon glass in these two forms as due only to a different cohesion and mechanical resistance. The multiplicity of surfaces, and the facility of movement in the powder, hasten its alteration in water.—*Comptes Rendus*, July 21, 1856, p. 117.

On the Nature of the Grease in the Wool of the Sheep.

By M. CHEVREUL.

The author has found in the grease of sheep's wool, and in that of the wool of the Alpaca, a considerable quantity of *oxalate of lime*; and this is the more remarkable as contrary to the general opinion; the grease of the Alpaca is acid, whilst that of the sheep, as has long been known, is decidedly alkaline. The grease also furnishes *silicate of potash.*

The author adds—

1. That the phocænic acid which he discovered in the oil of the Dolphins, and from which valerianic acid does not appear to differ, occurs in the grease, accompanied by an analogous acid, which may be new.

2. That in the grease of the sheep there is a considerable quantity of chloride of potassium, which is remarkable for its tendency to crystallize in octohedra, whilst the chloride of the human sweat, which is said to have sodium for its base, crystallizes in cubes.

3. That amongst other potash-salts, there are two of a very peculiar constitution, which form the greater portion of the saline matter of the grease.

4. That there exist at least five fatty matters in the grease, none of which have any analogy with those of mutton-fat. Amongst them he has obtained one in a crystalline form.—*Comptes Rendus*, July 21, 1856, p. 130.

Note on the Conversion of the Double Fluoride of Aluminium and Sodium (Cryolite) into Aluminate of Soda. *By* C. TISSIER.

If a mixture of—

Cryolite $[Al^2 Fl^3 3(NaFl)]$	500 grms.
Quicklime	250 grms.
Water......................	2 to 3 litres

be boiled for some hours, and filtered whilst boiling, and the filtrate be evaporated to dryness in a brass or silver basin, 100 grms. of a product are obtained, which, when analysed by M. Deville's process, gave the following results—

Aluminate of soda calcined at a red heat	0·900 grm.
Furnished alumina	0·312 grm.
Alumina per cent.	34·66 grms.
Containing aluminium......................	18·66 grms.

instead of 19·31 according to theory.

One of the most remarkable facts, as from it we may deduce important consequences as to the composition of cryolite, is the relation which exists between the quantity of aluminium which lime can thus cause to pass to the state of soluble aluminate, and the maximum quantity of this metal which has been obtained by the action of sodium upon cryolite. The quantity of aluminate of soda obtained with 250 grms. of lime and 500 grms. of cryolite is 100 grms., or one-fifth of the weight. The author has tried, by prolonging the operation and increasing the quantity of lime, to convert a larger proportion of the aluminium into aluminate, but without success. By this means hydrate of soda is obtained, containing only traces of alumina. By boiling the residue of the first operation with a fresh quantity of lime, he obtained 38 grms. of hydrated soda.

Thus about a third of the metal contained in cryolite is obtained both by this method and by the reduction of the mineral by sodium, which would lead to the supposition that the grouping of the molecules in cryolite may be very different from what is generally imagined.—*Comptes Rendus*, July 14, 1856, p. 102.

On some Sulphocyanides. *By* C. CLAUS.

Meitzendorff some time since published a valuable memoir on the metallic sulphocyanides*, in which however the compounds of iron with this radical were less completely examined than those of the other metals. The author proposes to fill up this gap.

Protosulphocyanide of Iron, $Fe, CyS^2 + 3HO$.—Concentrated hydrosulphocyanic acid is poured over small fragments of iron wire in a porcelain cup, and heated. The iron dissolves, with evolution of a rapid stream of a stinking hydrogen gas (resembling garlic in its odour), forming a bluish-green fluid, which reddens easily by oxidation when exposed to the air, and becomes partially converted into persulphocyanide of iron, but can be just as easily reduced again to protosulphocyanide. The solution is filtered when it is sufficiently concentrated, a thin iron wire is put into it, and a little free hydrosulphocyanic acid is added, and it is then heated until the red colour has given place to green. The cup is then placed over sulphuric acid *in vacuo*, and left to evaporate and crystallize. Pretty large, oblique rhombic prisms of a green colour are formed; these are of a much more intense green than the crystals of protosulphate or protochloride of iron. The salt is extremely sensitive to oxygen, forming persulphocyanide of iron, and becoming red. It is readily soluble in water, alcohol and æther, has a bitter inky taste, and decomposes readily when heated, evolving sulphuret of carbon, and forming mellonide of iron. For analysis, the crystals, as removed from the mother-liquor, must be dried as quickly as possible with a cloth and weighed, and then oxidized with very concentrated nitric acid in a long-necked flask furnished with a gas-tube. The oxidized fluid is diluted with water; the iron is first determined, and afterwards the sulphuric acid. The analysis gave—

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* Poggendorff's Annalen, lvi. p. 63.

Fe	23·56	28	23·83
2S	27·44	32	27·23
Cy	..	26	22·12
3½HO	26·74	31·5	26·82

As the sulphocyanides of the magnesia group mostly contain 3 equivs. of water, ½ equiv. has remained in consequence of imperfect drying, and the author considers the formula $FeCyS^2+3HO$ to be correct.

Persulphocyanide of Iron, $Fe^2, 3CyS^2+3HO$.—Meitzendorff did not succeed in obtaining this salt; Porret and Grotthous mention it as a crystalline compound. The salt is obtained as a dark brownish-red or nearly black crystalline mass by dissolving fresh hydrated peroxide of iron in concentrated hydrosulphocyanic acid, and evaporating the solution over sulphuric acid. It is obtained better crystallized in the following manner. 2 equivs. of anhydrous persulphate of iron, which is obtained as a snow-white body when sulphuric acid is distilled off from hydrated oxide of iron until all excess of acid is got rid of, is triturated with 1 equiv. of sulphocyanide of potassium, and the mixture is digested for some time with strong alcohol. The filtered deep red solution is evaporated over sulphuric acid. The salt is thus obtained in small rather indistinctly cubic crystals, of a deep blackish-red colour, with a slight brassy-green metallic lustre. It remains pretty well in the air without change, but in course of time loses a little sulphocyanogen, like persulphocyanide of copper, for the walls of the vessel in which it is kept become covered with a yellow coat. When heated, it behaves like protosulphocyanide of iron. It is readily soluble in water, alcohol, and æther. The latter extracts nearly the whole of it from an aqueous solution, and acquires a violet-purple-red colour. In the light, this solution behaves like perchloride of iron; it is reduced to green persulphocyanide of iron.

When a concentrated solution of the salt is mixed with much water, it loses its colour very quickly; but when the dilution is effected with an equal quantity of alcohol, its colour merely loses in intensity in proportion to the dilution. After the decolorization, a pale yellow, very finely divided body is formed in the fluid, which can be separated by filtration; this is a basic compound of peroxide of iron with a product of the decomposition of sulphocyanogen; but its quantity was too small to allow of its analysis. The filtered fluid is perfectly colourless, and contains free hydrosulphocyanic, hydrocyanic, and sulphuric acids; but its principal constituent is protosulphocyanide of iron, for ammonia throws down a dark precipitate of protoperoxide of iron, and nitric acid converts the protosulphocyanide into persulphocyanide, and again reddens the fluid. The presence of sulphuric acid may be ascertained by baryta-salts, and that of free hydrosulphocyanic acid by salts of iron. The hydrocyanic acid betrays itself by its odour. Persulphocyanide of iron therefore behaves towards water in the same way as persulphocyanide of copper. Meitzendorff also noticed this decomposition in his unsuccessful preparation of the persulphocyanide by heating hydrated peroxide of iron with dilute hydrosulphocyanic acid. Under these circumstances, however, the decomposition takes place very slowly. Sulphocyanide of potassium is however the most sensitive reagent for peroxide of iron, from its formation of the strongly coloured persulphocyanide of iron, even in very dilute solutions, provided these are acid. For acidification, muriatic acid must be employed, as other acids obscure the reaction.

As the reactions of this salt with iron may be modified by many circumstances, the author gives his observations upon this subject. The reaction can be detected in a fluid which contains $\frac{1}{10000000}$th of iron as peroxide, when the test-tube is looked into from above and held over a white surface. $\frac{1}{5000000}$dth of iron gives an intense rose-red reaction. This reaction is not prevented by dilute acids, especially monobasic acids, such as muriatic, sulphuric, nitric, and boracic acids, or the fatty acids. Much concentrated nitric acid decolorizes the fluid by decomposing the sulphocyanogen. Polybasic acids, on the contrary, such as tartaric, malic, lactic, and particularly oxalic and phosphoric acids, deprive the fluids of their colour. A considerable addition of muriatic acid usually reproduces the original colour, except with phosphoric and oxalic acids. Salts with an alkaline reaction of course also prevent the reaction. Nitric acid acts in the same way as muriatic acid, within certain limits of dilution; but it may give rise to great mistakes, from its capability of preventing the reaction when iron is present, or producing the reaction of iron when it is absent. When a small quantity of sulphocyanide of potassium is added, a strong acid immediately destroys the persulphocyanide of iron by oxidizing the sulphocyanogen; and the same acid, with a larger quantity of sulphocyanide of potassium, gives a strong colour similar to that of the iron reaction, although no iron may be present; this however is soon converted into citron-yellow, the action of the nitric acid in this case producing a body similar to Liebig's sulphocyanogen, the formation of which commences with a red colour. The analysis of persulphocyanide of iron gave—

2Fe	21·01	56	21·75
6S	37·56	96·5	37·47
3Cy	..	78	30·29
3HO	11·00	27	10·49

Sulphocyanide of Cobalt, Co, CyS^2, was only obtained by Meitzendorff as a crystalline mass, whilst Grotthous and the author prepared it in beautiful dark violet prisms.

Buckton has published a valuable memoir upon the double sulphocyanides[*], but has not mentioned that the principal material from which he prepared his salts, the sulphocyanide of potassium and platinum, was previously known. For these compounds Buckton has adopted Graham's radical theory of the cyanogen compounds of iron, although they cannot be compared with them. There is, in these cases, no reason to admit the existence of the radicals $Cy^2 S^4$ and $Cy^3 S^6$[†], as they all belong to the series of double salts, and behave like the double chlorides, bromides, and iodides of platinum. The sulphocyanogen, and the other constituents contained in them, may be determined by the ordinary reagents, as for instance in persulphocyanide of potassium and platinum, the platinum by sulphuretted hydrogen, the sulphocyanogen by silver-salts, and lastly the potash by perchloride of platinum. These salts consist of equal equivalents of the two metallic sulphocyanides, like those double cyanides for which it has never been thought necessary to adopt any radical. They may be converted by strong acids into hydrosulphocyanic acid and salts which contain no sulphocyanogen. Persulphocyanide of platinum in combination with hydrosulphocyanic acid, or platino-hydrosulphocyanic acid, is not a stronger acid than hydrosulphocyanic acid itself, whilst in the cyanides in which we admit radicals the metallic radicals are stronger acids than hydrocyanic acid. All these reasons go to show that the supposition of radicals in this case has no sufficient foundation. Still less do these compounds agree with the radical theory as established by Liebig for the cyanogen compounds. Buckton states that the persulphocyanide of potassium and platinum is decomposed in a remarkable manner by nitric acid, without giving any particulars about it. The author states that very concentrated fuming nitric acid, containing hyponitric acid, acts very violently upon a concentrated solution of this salt; evolution of nitrous oxide gas and carbonic acid takes place, and an orange pulverulent body separates, which gradually loses its colour by oxidation, and at last becomes quite colourless. In the coloured state it is a compound of the white body with Liebig's sulphocyanogen; in the white condition it is a platinum-acid, consisting of platinum, cyanogen and oxygen. To obtain this quite free from sulphur, it must be digested for eight days with constantly renewed nitric acid, until a sample burnt with carbonate of soda and nitrate of potash gives no reaction of sulphuric acid. In this oxidation of the persulphocyanide of potassium and platinum, no platinum goes into the solution; this contains sulphate of potash, free sulphuric acid and nitric acid. The white acid body is nearly insoluble in water; when moistened with water, it acts as an acid upon blue paper; it is not acted upon by stronger acids, and dissolves in concentrated solution of potash, from which it is again thrown down by acids. The results of an imperfect analysis led to the formula $Pt^2 Cy + O$, so that the body might be regarded as a conjugate compound of platinum and cyanic acid.—Liebig's *Annalen*, July 1856, p. 48.

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[*] Quart. Journ. Chem. Soc., viii. p. 22.

[†] If the sulphocyanide of potassium and rhodium $= 3KCyS^2 + Rh^2, 3CyS^2$ were prepared, we should have to admit a radical, $Cy^6 S^{12}$.

On the Behaviour of Iodine towards Sulphite of Soda.

By Dr. BRAUNE.

For the preparation of hydriodic acid by Méné's process, in accordance with the equation $NaO, SO^2 + HO + I = NaO, SO^3 + HI$, the following proportions are given in Gmelin's 'Handbuch*,' 6 parts of crystallized sulphite of soda, 3 parts of iodine, and 1 part of water. The author found that with these proportions sulphurous acid was produced, perfectly free from iodine, so that the iodine had expelled sulphurous acid. The author supposes this to be caused by some impurities in the commercial iodine, and to ascertain whether this is the case he intends to examine the residue.—*Chemisches Centralbl.*, July 16, 1856, p. 528.

Action of the Chlorides and Bromides of Phosphorus upon Glycerine.

By MM. BERTHELOT *and* DE LUCA.

This memoir includes three parts,—1st, the action of the chlorides of phosphorus upon glycerine; 2ndly, the action of the bromides of phosphorus upon glycerine; and 3rdly, the action of ammonia, tin, and perbromide of phosphorus upon dibromhydrine.

I. The action of the chlorides of phosphorus upon glycerine is similar to that of muriatic acid; the principal bodies to which it gives origin are, dichlorhydrine, $C^6 H^6 Cl^2 O^2$; monochlorhydrine, $C^6 H^7 ClO^4$; and epichlorhydrine, $C^6 H^5 ClO^2$. These substances having already been studied by M. Berthelot, the authors have not further examined this reaction.

II. The two bromides of phosphorus act in the same manner upon glycerine; they give rise to several bromhydrines, all comprised under the general formula—

$$n\,C^6 H^8 O^6 + m\,HBr - p\,H^2 O^2.$$

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* Fifth edition, p. 702.

The authors have succeeded in isolating the following compounds, principally by distillation, sometimes with the naked fire and under ordinary pressure, and sometimes on the oil-bath *in vacuo*:—

1. *Monobromhydrine*, $C^6 H^7 BrO^4 = C^6 H^8 O^6 + HBr - 2HO$.
2. *Epibromhydrine*, $C^6 H^5 BrO^2 = C^6 H^8 O^6 + HBr - 4HO$.
3. *Dibromhydrine*, $C^6 H^6 BrO^2 = C^6 H^8 O^6 + 2HBr - 4HO$.
4. A neutral body, volatile above 392° F., which appears to be a *hemibromhydrine*, $C^{12} H^9 BrO^4 = 2(C^6 H^8 O^6) + HBr - 8HO$, analogous to the iodhydrine previously described by the authors.
5. A crystallized, black, fixed substance, slightly soluble in æther, presenting the composition of a *hexaglyceric bromhydrine*,

$$C^{36} H^{27} BrO^{14} = 6(C^6 H^8 O^6) + HBr - 22HO.$$

6. Various liquid substances, volatile *in vacuo* at 392° F. and upwards, which also appear to be bromhydrines, but which could not be purified.
7. A brominated compound, volatile between 149° F. and 152°·6 F., the odour of which resembles that of allylic æther. This body is in very small quantity.
8. Acroleine.
9. A white, volatile, crystallized body, $C^{12} H^9 Br^2 P$, which may be represented as a compound of epibromhydrine and phosphuretted hydrogen, $C^{12} H^9 Br^2 P = 2(C^6 H^5 BrO^2) + PH^3 - 4HO$.

Monobromhydrine, $C^6 H^7 BrO^4$, is a fluid, oily, neutral compound, with a penetrating and aromatic taste; when heated over the naked fire, it does not distil without decomposition, but distils *in vacuo* at about 356° F. under a pressure of between 0·01 and 0·02 millim. When treated with potash at 212° F., it is decomposed, and reproduces bromide of potassium and glycerine; a small quantity of a black substance is formed at the same time.

Epibromhydrine, $C^6 H^5 BrO^2$, is obtained in large quantity by the action of the bromides of phosphorus upon glycerine. It is a neutral mobile fluid, with an ætherial odour and a penetrating taste; its density is = 1·615 at 56°·4 F., and it boils at 273°·4 F. The density of its vapour, determined at 352°·4 F., was found = 5·78. The theoretical number corresponding with 4 vols. would be 4·66. It is probable that this density was determined at a point to near that of ebullition, but the ready decomposition of epibromhydrine forbade a higher temperature. Epibromhydrine, heated to 212° F. with moist oxide of silver, produces bromide of silver and glycerine; potash decomposes it at 212° F. in the same way.

When treated with perbromide of phosphorus, epibromhydrine furnishes the same compounds as dibromhydrine. At the same time a portion of the epibromhydrine is destroyed, with formation of a black matter and evolution of a mixture of oxide of carbon, carbonic acid, hydrogen, and propylene. It will be observed that epibromhydrine is isomeric with chloride of propione.

Dibromhydrine, $C^6 H^6 Br^2 O^2$, is the most abundant product of the reaction of the bromides of phosphorus upon glycerine. It is a neutral liquid, with an ætherial odour, analogous to that of the chlorhydrines. Its density is$=2{\cdot}11$ at 50° F. It boils at 426°·2 F. When treated with potash at 212° F., it forms bromide of potassium and glycerine.

III. By the action of ammonia, tin, and perbromide of phosphorus upon dibromhydrine, the authors have obtained *glycerammine*, $C^6H^9NO^4$, and *tribromhydrine*, $C^6H^5Br^3$.

1. The action of ammonia varies according as the dibromhydrine is pure or dissolved in alcohol. If a current of gaseous ammonia be passed into pure dibromhydrine, an abundant crystalline deposit is rapidly formed; the mass soon becomes heated and coloured, and changes into a mixture of hydrobromate of ammonia and an amide substance, which is insoluble in water and all other solvents. According to analysis, this body contains $C^{12}H^{12}BrNO^4$. Its formation is explained by the following equation:—

$$2(C^6H^6Br^2O^2)+4NH^3=C^{12}H^{12}BrNO^4+3(NH^3, HBr).$$

On the other hand, if a current of gaseous ammonia be passed into an alcoholic solution of dibromhydrine, hydrobromate of ammonia is obtained with the hydrobromate of a new base, *glycerammine*, $C^6H^9NO^4=C^6H^8O^6+NH^3-2HO$. This base is liquid, and very soluble in water and æther. Æther does not abstract it from its aqueous solution; but if its hydrobromate be decomposed by an extremely concentrated solution of potash, the glycerammine separates in an oily form; on the addition of a little water, it dissolves again. It produces a deliquescent, or rather extremely hygrometric chloride. This salt dissolves with difficulty in absolute alcohol. When heated, it blackens and decomposes, evolving a strong odour of burnt horn; its aqueous solution is not precipitated by bichloride of platinum; but still if the two solutions be concentrated *in vacuo*, and absolute alcohol, either pure or mixed with æther, be added to them, the double salt of platinum and glycerammine, $C^6H^9NO^4, HCl, PtCl^2$, is obtained in the form of little orange grains.

2. Dibromhydrine, treated with metallic tin at 284° F., forms bromide of tin and a peculiar compound, which is insoluble in water, soluble in æther, and contains no tin. The authors could not form any crystallizable compound of this body.

3. If a mixture of dibromhydrine or epibromhydrine and perbromide of phosphorus be distilled, the product of the reaction, when treated with water and redistilled, furnishes,—1st, between 347° and 356° F., tribromhydrine, $C^6H^5Br^3=C^6H^8O^6+3HBr-6HO$; and 2ndly, towards 392° F., a peculiar compound, $C^6H^7Br^3O^2$, which may be regarded either as a hydrate of tribromhydrine, $C^6H^5Br^3+2HO$, or as a hydrobromate of dibromhydrine, $C^6H^6Br^2O^2+HBr$.

Tribromhydrine, $C^6H^5Br^3$, is a heavy liquid, volatile about 356° F., slowly decomposable by water, and slightly fuming in contact with the air. In the formation of this compound all the oxygen of the glycerine is eliminated in the form of water. Tribromhydrine belongs to the third series of glyceric compounds, and corresponds to the natural fatty bodies; but it is distinguished therefrom in not being neutral like the other bodies of the third series, a circumstance which is easily explained by the great chemical energy of hydrobromic acid, which forms seven-eighths of the tribromhydrine.

These facts certainly once more establish the existence of three distinct series of glyceric compounds, formed by 1 equiv. of glycerine with 1, 2, and 3 equivs. of acid; they show that besides these three fundamental series there are compounds formed by the union of 1 equiv. of acid with several equivalents of glycerine, the analogues of which occur amongst the natural proximate principles with a glucoside base. Lastly, the existence of glycerammine, agreeably to the analogies of glycerine with alcohol, furnishes the first example of an alkaloid formed by a saccharine substance.—*Comptes Rendus*, July 14, 1856, p. 98.

On Sulphocyanide of Benzoyle. By H. Limpricht.

When equal equivalents of chloride of benzoyle and sulphocyanide of potassium are brought in contact, a strong evolution of heat takes place, with an odour of sulphuret of carbon. On distillation, a slightly coloured fluid passes, which becomes perfectly colourless after a few rectifications, boils at 376° F., and possesses all the properties of benzonitrile. Its analysis also furnished numbers corresponding with this substance:—

C	81·0	14	= 84	81·5
H	5·1	5	5	4·8
N	13·4	1	14	13·6

The decomposition of the sulphocyanide of benzoyle, which is probably formed at first, is shown by the following equation:—

$$2(C^{14}H^{5}O^{2}, C^{2}NS^{2}) = 2C^{14}H^{5}N + C^{2}O^{4} + C^{2}S^{4}.$$

Sulphocyanide of benzoyle. Benzonitrile.

Liebig's *Annalen*, July 1856, p. 117.

Note on a Double Hyposulphite of Soda and Copper.
By W. Schütte.

When a tolerably concentrated solution of hyposulphite of soda is added to an ammoniacal solution of a salt of copper, a violet-blue salt is deposited. It is formed in the cold, but more rapidly with the aid of heat, in proportion as the ammonia is volatilized. It crystallizes in small prismatic needles, of which the crystalline form could not be exactly determined. The same salt is obtained by pouring a solution of hyposulphite of soda into a solution of a copper-salt, and adding the ammonia afterwards, or by treating an ammoniacal solution of protochloride of copper with hyposulphite of soda. In these two cases the blue salt is formed by absorbing oxygen from the air, and generally presents a deeper tint than the same salt obtained by the first method, especially in operating with heat or with very concentrated solutions.

The analysis showed, besides hyposulphurous acid, soda, ammonia, and peroxide of copper, a considerable quantity of protoxide of copper. It is very probable that the protoxide and deutoxide of copper replace one another, which explains the difference in the tints of the salt from different operations and in the results obtained by quantitative analysis. The salt is anhydrous and permanent in the air. When heated to 212° F., it becomes brown and evolves ammonia, but lost no water. At a higher temperature, ammonia, sulphite of ammonia, and sulphur are disengaged, and a black mass containing sulphuret of copper and sulphate of soda is formed. The salt is decomposed by cold water. It dissolves in hot water, but when the solution is heated for some time, the whole of the copper is precipitated in the form of sulphuret. Acids decompose it at ordinary temperatures, with precipitation of sulphur and evolution of sulphurous acid, which proves the presence of hyposulphurous acid.

Its quantitative analysis is difficult from the slight stability both of the acid and the base, and the readiness with which the copper is sulphuretted by hyposulphurous acid. The sulphur, copper, soda, and ammonia were determined by the well-known processes; but the determination of the relative proportions of protoxide and peroxide of copper presented peculiar difficulties. They had to be converted by sulphuretted hydrogen into the corresponding sulphurets, the analysis of which gave a clue to the relative proportions of the oxides. The average of several analyses agreed best with the following formula:—$4S^2O^2, NaO + 3S^2O^2, Cu^2O + S^2O^2, CuO + 4NH^3$.

		Calculated.
NH^3 =	9·897	8·3
NaO	15·758	14·9
S^2O^2	47·689	46·2
Cu^2O	22·63	25·8
CuO	4·007	4·8

The difference between the quantity of protoxide of copper found and calculated is explained by observing that the substitution of protoxide of copper for peroxide requires the replacement of 1 equiv. of copper by 2 equivs. of the same metal. The following notation represents the constitution of this salt at once in a simple and rational manner:—

$$S^2O^2, NaO + S^2O^2 \left\{ \begin{matrix} Cu^2O \\ CuO \end{matrix} \right\} + NH^3.$$

Comptes Rendus, June 30, 1856, p. 1267.

On Getah Lahoe. *By* Prof. KAISER.

Under the name of Getah Lahoe, a substance has recently been brought from the East Indies to Amsterdam. It was given out to be gutta-percha, with which however it has no similarity. It is rather a waxy material, united with soft resin.

The substance is of an ashy-gray colour, somewhat porous, fatty to the touch, light, and swims on water. Its specific gravity at 52° F.=0·963. Between the warm fingers it may be kneaded like wax, but it is harder and more brittle than that substance. It may be easily broken in pieces, and large fragments may be broken by the hands. On the freshly broken fibrous surfaces it exhibits a sticky moisture, which speedily dries in the air, and an opalescent fatty appearance, comparable with that of dried milk sap. With the pestle and mortar it may be triturated to a coarse coherent powder, and exhibits no foreign organic or inorganic constituents; during trituration it evolves a caseous odour. In large pieces its odour has a distant resemblance to that of honey. In lukewarm water it becomes sticky; after kneading, compression, and drying in the air, it forms a grayish-green brittle mass. It melts at a temperature of 107° F. with evolution of gas, and an exhalation which reddens litmus, and has an odour like that of wine-lees. In fusing, it becomes a clear fluid, from which a black powder separates, and solidifies to a wax-like mass.

When fused in a retort and long heated, heavy white fumes are produced, which could only be carried over into the neck of the retort by means of the spirit-lamp, and when the heat was reduced, condensed into a stearine-like mass with an empyreumatic odour, which dissolved in æther to a brownish fluid. When melted upon water, it is sticky like turpentine, and can be drawn out into long threads. Owing to its ready fusibility, it burns with a brightly luminous but very smoky flame, when furnished with a wick and ignited. It does not dissolve in water and alcohol, either at ordinary temperatures or at a boiling heat. Absolute alcohol takes up about one-tenth of a very tenacious constituent. Æther however dissolves the whole of it except about one-hundredth of a blackish-brown powder, and furnishes on evaporation a white, fatty, wax-like substance, which separates like a coagulum as soon as the evaporation of the æther commences. It is equally soluble in turpentine and rectified naphtha. Sulphuret of carbon converts it into a white flocculent material without dissolving it. Melted with an equal quantity of sulphur, it forms a yellowish-gray plastic mass, without undergoing any further change. When kept melted for a long time over water, it becomes grayish-green, sticky, and like softened wax. It leaves 0·005 of a calcareous ash.—*Kunst- und Gewerbebl. für Bayern,* 1856, p. 109.

ANALYTICAL CHEMISTRY.

New Methods of Assaying for Lead and Antimony. By A. Levol.

The author has endeavoured to assay the ores of lead and antimony by means of the cyanides. Mixtures of commercial cyanide of potassium and anhydrous ferrocyanide of potassium appear to be best adapted for the purpose. The sample is heated with the mixture to a dull red heat in an iron crucible. The following are experiments with variable quantities of the fluxes or reducing agents. The ferrocyanide of potassium is anhydrous:—

		Parts.	Lead.	Loss of lead per cent.
1.	Pure galena	100		
	Ferrocyanide of potassium ..	50	80·0	6·55
	Cyanide of potassium	50		
2.	Galena	100	84·0 to	2·55 to
	Ferrocyanide of potassium ..	100	84·5	2·00
	Cyanide of potassium	50		
3.	Galena	100	Becomes greatly inflated, and the experiment accordingly failed, as also 4 & 5.	
	Ferrocyanide of potassium ..	100		
	Cyanide of potassium	100		
4.	Galena	100		
	Ferrocyanide of potassium ..	150		
	Cyanide of potassium	50		
5.	Galena	100		
	Ferrocyanide of potassium ..	50		
	Cyanide of potassium	50		
	The mixture was also covered with cyanide of potassium	50		

The mixture No. 2 is the best. It is but little inflated, and gives a result which is correct within 2 to 2·5 per cent.

To ascertain what influence the presence of other metallic sulphurets may have upon this process, the author experimented upon the following mixture:—

		Lead.	Loss of lead per cent.
Galena....................	100	80	5·05
Blende....................	50		
Ferrocyanide of potassium	100		
Cyanide of potassium........	50		

Here therefore the volatilization of the zinc carried a good deal of lead with it. A mixture of—

Galena	100
Sulphuret of antimony	50
Ferrocyanide of potassium	100
Cyanide of potassium..........	50

furnished a brittle regulus indicating the produce of 92 per cent. of galena; it must therefore have contained at least 7 per cent. of antimony. With lead ores containing antimony therefore the new method cannot be employed.

The author then assayed ore of antimony in a similar way. It did not succeed with cyanide of potassium alone. A mixture of—

Sulphuret of antimony	100
Ferrocyanide of potassium	200

was covered with 50 parts of powdered cyanide of potassium. A regulus of 72 parts was obtained from an ore with an actual amount of 72·77

The superiority of this process over the ordinary one depends upon the extremely fine division of the iron which is brought into contact with the metallic sulphurets by means of the ferrocyanide of potassium. A second advantage is, that a much lower temperature is sufficient.—*Ann. de Chim. et de Phys.*, 3 ser. xlvi. p. 472.

On a peculiar Behaviour of Nitrogenous Bodies in the Blowpipe Flame. By A. Vogel, Jun. *and* C. Reischauer.

If the tip of a sharply-blown blowpipe-flame be directed upon a piece of the stem of a feather, the border round a reddish nucleus becomes distinctly green. The same takes place with other nitrogenous bodies, such as horny tissue, gelatine, albumen, yolk of egg, chondrine and chitine, and also with a series of organic bases, such as quinine, cinchonine, strychnine, veratrine and urea. In the dark the green is also observed on the red flame of cyanogen, by the introduction of nitric oxide gas into a flame, and by the combustion of ammonia. The green colour of the flame appears to be peculiar to nitrogen when it escapes from a compound containing oxygen or hydrogen.—Buchner's *Neues Repertorium*, v. p. 153.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Paris Blue. By G. E. Habich.

Paris blue is equally well adapted for a body colour as for mixtures, from its being readily ground up and possessing a considerable covering-power. With chrome-yellow it gives the admired green cinnabar, or the so-called sap-green. The author recommends the following processes for the preparation of this colour, as being cheaper than the old methods:—

1. *Preparation with Chlorine* (nitromuriatic acid).—As in the old processes, the white precipitate is first prepared with ferrocyanide of potassium and sulphate of iron. The latter must as far as possible be free from the persalt. For this purpose metallic iron is kept in the tubs in which the solution of sulphate of iron is set to clear, and this also precipitates any copper that may be in the solution. It is also necessary that the precipitation should be effected in the solution of ferrocyanide of potassium whilst still hot, in order to avoid as far as possible the absorption of oxygen, and the premature blue coloration of the precipitate produced thereby. For the same reason the filtration of the white precipitate is effected at once and as quickly as possible. It is only the blue produced by the action of chlorine, nitric acid, &c. upon the white precipitate that has the intensity of colour required by the colour manufacturers, whilst the precipitate which has become blue in the air, even when the intermixed hydrated peroxide of iron has been extracted from it by muriatic acid, always furnishes a colour with less body, which is never sufficient for the manufacture of green cinnabar.

When to 100 lbs. of ferrocyanide of potassium 90 lbs. of sulphate of iron are employed, a drop of the solution of iron no longer produces a precipitate in a filtered portion of the fluid; the white precipitate has then carried a quantity of ferrocyanide of potassium mechanically mixed with it to the bottom, which can be extracted by washing with water. This quantity of the expensive material would thus be partially lost, and the best way to avoid this loss is the following. The iron solution is added, with constant stirring, until no further precipitate is produced, and then a ninth part of the quantity of solution employed. If the mixture be now stirred for a quarter of an hour, there is a certainty that all the intermixed ferrocyanide of potassium is decomposed.

To give a blue colour to this precipitate, which is allowed to drain until it forms a thick paste, by the agency of chlorine, a mixture of muriatic and nitric acids, prepared on the previous day, is employed. The quantity to be mixed must of course depend on the quantity of anhydrous acid contained in the commercial acids. The mixture is made so that it may contain 54 parts by weight of anhydrous nitric acid, and 36½ parts of anhydrous muriatic acid. To colour the white precipitate, such a quantity of this mixture is employed that for every 100 parts of ferrocyanide of potassium made use of in the precipitation, there may be 10$\frac{7}{10}$ parts of anhydrous nitric acid in the mixture. Thus if we have a nitric acid of 30° B. (=spec. grav. 1·256 according to the tables in Graham's Manual), and a muriatic acid of 23° B. (=spec. grav. 1·185), the former will contain, according to Ure's tables, 35$\frac{4}{10}$ per cent. of nitric acid, and the latter 37½ per cent. of muriatic acid. The mixture would be prepared with 100 lbs. of this nitric acid (containing 35$\frac{4}{10}$ lbs. of anhydrous acid), and 64$\frac{2}{10}$ lbs. of the muriatic acid (containing 23$\frac{2}{10}$ lbs. of anhydrous acid); and of this mixture 49 lbs. would be sufficient to colour the precipitate from 100 lbs. of ferrocyanide of potassium. This quantity is gradually added, with constant stirring, to the white precipitate contained in wooden tubs.

To determine whether the proper colour is attained, a little of the coloured precipitate is put into a glass, and a drop of the acid mixture is added to it. Of this sample a drop is rubbed upon white paper, and compared with a sample of the colour as it exists in the tub. If the addition of acid has increased the intensity of the colour, too little of the acid mixture has been used, and a further quantity must be added. But if the sample has acquired a greenish tinge, either the exact quantity or too much of the mixture has been used. To determine this, a fresh sample is put into the glass, and a drop of the white precipitate suspended in water is put in. If the intensity of the colour be increased, too much of the acid mixture has been employed, and this error is repaired by the addition of small quantities of the white precipitate until the highest degree of intensity is attained. The colour is then washed, &c. in the usual way.

2. *Process with Perchloride of Iron.*—In this the blue coloration of the white precipitate produced by ferrocyanide of potassium and sulphate of iron is effected by a solution of perchloride of iron; this is converted into protochloride of iron, which then serves in place of an addition of sulphate of iron. To prepare the perchloride of iron, an iron ore must be obtained as free as possible from alumina and lime, but it is of no consequence whether it be a red or a brown ironstone. If an iron ore of this kind cannot be procured, the residue from the manufacture of oil of vitriol, well known under the

names of caput mortuum, coleothar, English rouge, &c., may be employed. The disposable oxide of iron from either of these sources is put in a finely powdered state into a wooden tub lined with thin sheet lead, and the ordinary muriatic acid (such as is furnished by the soda manufacturers) is poured over it. The mixture is allowed to stand for several days, with frequent stirring, and the supernatant fluid, which must have become saturated with oxide of iron, is drawn off into another vessel, in which it may become perfectly clear. This solution of perchloride of iron is kept constantly ready for the production of the blue colour.

A precipitate is prepared with ferrocyanide of potassium and sulphate of iron in the way already described; this is filtered, and the pasty residue is heated to boiling in a copper pot, when it is emptied into a tub standing under the crane of the kettle, and mixed with the perchloride of iron, stirring constantly until the highest intensity of colour is obtained. In this operation there is no occasion to be so careful as in the production of the blue colour with nitromuriatic acid, as an excess of perchloride of iron is not injurious to the purity of the colour. Perchloride of iron is therefore added until a slight excess of it is present, that is to say, until a filtered portion of the fluid gives a blue precipitate with a drop of solution of ferrocyanide of potassium. When this point is attained, the fluid is either filtered off, or the colour is merely allowed to settle, and the clear fluid is drawn off. This fluid, as already mentioned, is principally a solution of protochloride of iron. To convert it entirely into this, it is poured upon fragments of old iron, when it will soon serve in place of sulphate of iron for the precipitation of the ferrocyanide of potassium,—a great advantage in this process of manufacture.

3 *Process with Perchloride of Manganese.*—The commercial value of the ores of manganese depends upon the amount of peroxide of manganese which they contain. The ordinary ores however generally contain a considerable quantity of oxide of manganese, which can be extracted from them by cold muriatic acid; and this will of course increase their value, and at the same time furnish a new material for this manufacture. The process is exactly the same as with perchloride of iron; but as the supernatant solution of protochloride of manganese is of no particular value, the employment of superfluous perchloride in the production of the blue colour must be carefully avoided; and it is necessary, during the gradual addition of this agent, to determine the exact point at which the greatest intensity of colour is attained by the comparison of samples. In consequence of the ready decomposability of the perchloride of manganese, this comparison is the only way by which the object can be attained. The other manipulations are as usual.

The residue of the ore, after treatment with muriatic acid, is of course carefully washed and dried before it is sold as peroxide of manganese.

4. *Process with Chromic Acid.*—This method, like the preceding, is only to be recommended under certain circumstances, as the chrome-salts produced are not of much value. 10 parts by weight

of red chromate of potash are dissolved in about 10 times their weight of hot water, and after cooling mixed with 13½ parts by weight of English sulphuric acid. This mixture is preserved for use in well-closed carboys. When it is to be employed, the precipitate from ferrocyanide of potassium and sulphate of iron is boiled, and the solution of chromic acid is added to it until the greatest intensity of colour is produced.

In the preparation of Paris blue in many manufactories, the ferrocyanide of potassium is simply precipitated by the addition of sulphate of iron as long as a precipitate is formed, the mixture rendered blue by the action of the air, and washed. By this means a considerable loss of the valuable ferrocyanide of potassium takes place. It is established by exact chemical experiments, that 50 per cent. of the ferrocyanide of potassium employed in the precipitation of a protosalt of iron enters with the whole of the potash into the white precipitate, and that the greater part of this dissolves again when the precipitate is rendered blue by the action of the air, and is thus lost during washing. This loss is avoided, at least for the most part, when the blue is produced by any of the above methods, and no loss need be sustained if the filtrates from the white precipitate be collected and precipitated with sulphate of iron.—*Polytechn. Journ.*, cxxxviii. p. 295.

PATENTS.

Patent granted to F. Uchatius, *for an Improvement in the Process of manufacturing Cast Steel.*

The object of this invention is to reduce the cost of manufacturing cast steel by œconomizing the labour of the process. To this end, the inventor takes pig iron of the purest quality, and melts it in a suitable furnace, and while in a molten state he runs the metal into cold water, and thereby reduces it to granulated iron. It is now in a suitable condition to undergo the process which will convert it into cast steel. This process is founded on the well-known fact, that cast iron enwrapped or surrounded by any oxygenized materials, and subjected to a cementing heat for a given time, will yield up a portion of its carbon, which will combine with the oxygen driven off from the surrounding materials, and form carbonic oxide or carbonic acid gas. If this process is interrupted before the completion of the process, a partially decarbonized iron will result, the surface of which will have been converted into a pure iron, while the interior parts remain unchanged; or, in other words, the progress of the decarbonizing action will depend on the amount of metallic surface brought into contact with the oxygen-yielding material with which the iron is surrounded. In order therefore to expedite this operation, the pig iron is reduced, as before mentioned, to a granulated state; and further to œconomize fuel and labour, the heat required for effecting the decarbonization of the iron is employed to reduce the metal, when sufficiently decarbonized, to a molten state; and thus by one and the same heating it is converted into cast steel, which only needs to be forged to prepare it for the market. The granulated iron is mixed with about 20 per cent. of roasted pulverized sparry iron ore and 4 per cent. of fire-clay, and then placed in fire-clay crucibles, and subjected to heat in a cast-steel blast-furnace of an ordinary construction. By thus subjecting the granules of iron in presence of the sparry iron ore to a melting heat, the enwrapping oxides will first effect a partial decarbonization of the granulated iron, which decarbonization will be limited in amount according to the size of the granules operated upon; and by reason of the continued application of heat, the iron will melt and separate (with the assistance of the melting residues of sparry iron ore) from the impurities with which it was mixed, and also bring down with it a portion of the iron contained in the sparry iron ore, thereby increasing the yield of cast steel by about 6 per cent.

The quality of the steel is capable of being by this process considerably modified. Thus the finer the pig iron is granulated, the softer will be the steel made therefrom. The softer sorts of welding cast steel may be obtained by an addition of good wrought iron in small pieces, and the harder qualities by adding charcoal in various proportions to the before-mentioned mixture.—Dated October 1, 1855.

Patent granted to R. A. Tilghman, *for Improvements in the Manufacture of Alkalies and Alkaline Earths.*

This invention consists in decomposing the sulphates of the alkaline earths by exposing them at a high heat alternately to the action of deoxidizing and oxidizing agents, whereby the sulphuric acid is gradually driven off and the alkaline bases are left in a free state. By exposing sulphate of baryta, for example, at a high heat, to a current of deoxidizing gas, part of its sulphur is carried off in a gaseous state, while part remains in combination as sulphuret of barium. By now admitting fresh air to oxidise this sulphuret, part of its sulphur again comes off in a gaseous state, while a part oxidizes, reproducing sulphate of baryta. By repeating the alternations of deoxidation and oxidation a sufficient number of times, the whole of the sulphur may be driven off. The operation is always finished by a prolonged oxidation, so as to destroy any sulphuret which might otherwise contaminate the product. When either the sulphate used, its sulphuret, or its base are fusible at the heat employed, it is mixed with magnesia, or other suitable infusible material, so as to preserve the mass in a porous state. The gaseous compounds of sulphur given off by this operation may be employed, if desired, to make sulphuric acid or sulphates by known processes. The alkalies, potash, and soda are manufactured by digesting the baryta or strontia, produced by the above process, with a solution of sulphate of potash or of soda.

In carrying out this invention, in order to decompose the sulphate of either baryta or strontia, it is ground to fine powder, and mixed with half its weight, or less, of magnesian lime. That which has had part of its lime removed by washing or acids is preferred: a smaller portion of it will suffice than of the unwashed. The mixture is moistened with water, moulded into bricks, and burnt in a kiln, such as is used in burning fire-bricks. When the bricks have reached a bright red or yellow heat, the decomposing process is commenced by throwing fresh fuel on all the fires, and if needful partially closing the dampers, so as to render the atmosphere in the kiln strongly deoxidizing. A great quantity of sulphur then escapes as sulphurous acid, sometimes as sulphuretted hydrogen, and perhaps in other forms. This evolution of sulphur gradually becomes less strong, and when it has almost ceased the atmosphere of the kiln is made oxidizing by the admission of fresh air through suitable openings above the level of the fuel; and by opening the dampers, another discharge of sulphurous acid, as copious, if not more so than the first, now takes place, and on its gradual decline a deoxidation is again effected as at first. By this repeated alternation of deoxidation and oxidation, the whole of the sulphate is decomposed. The sulphurous smell of the escaping gases is a sufficient guide to the workman as to the proper time for changing the nature of the atmosphere in the kiln; and when such a smell is no longer produced by the alternations, it is a sign that the charge is sufficiently decomposed, and ready for the prolonged finishing oxidation. When this is ended, all the remaining fuel should at once be removed from the fireplaces, as, if left to die out gradually during the cooling of the kiln, a portion of the caustic baryta or strontia becomes carbonated by it. Care should be taken to avoid, as much as possible, allowing the siliceous ashes of the fuel to be carried over by the draught among the bricks. The use of a fan-blast to the fires will be found very convenient (though not at all necessary) in effecting the desired changes of atmosphere in the kiln; when used, the fuel can be kept very deep upon the bars, so that carbonic oxide can be employed as the chief agent in deoxidation. The above process can be carried on in reverberatory furnaces, if preferred, in which case little or no magnesia would be required in the charge; but the above process is considered more advantageous.

When the sulphate of lime is to be decomposed, it does not need the addition of magnesia to render it porous and infusible in the fire, as its reduction takes place at a lower heat than that required for the sulphates of baryta or strontia. The sulphate of magnesia should first be carefully dried from all its water of crystallization, and placed in a fire-clay retort, like those used for gas, and then very gradually heated to redness, having a current of deoxidizing gas passing through it from the commencement of the heating. The same alternation of deoxidation and oxidation as before is to be used, but the decomposition is much more easily effected. It is preferred to keep the heat low in this operation, especially at the beginning, so as to avoid all chance of fusing the sulphate of magnesia. The caustic magnesia then produced is soft and impalpable, but if a strong heat is used it becomes harsh and gritty.—Dated August 3, 1855.

THE CHEMICAL GAZETTE.

No. CCCXXXV.—October 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Glycol or Diatomic Alcohol. By A. Wurtz.

It is well known that ordinary alcohol forms æthers by reacting upon 1 molecule of acid. M. Berthelot has shown that glycerine combines with 3 molecules of a fatty acid to form the natural fatty bodies. Between alcohol and glycerine therefore there is a difference analogous to that which separates a monobasic from a tribasic acid; and if spirit of wine be a monoatomic, glycerine may be regarded as a triatomic alcohol.

Assuming the existence of compounds intermediate between alcohol and glycerine, the molecule of which would be diatomic, the author has succeeded in forming by synthesis an alcohol of this nature, which he names *glycol*, because it approaches in its properties both alcohol and glycerine, between which it should be placed. This will probably become the type of a series of analogous compounds, as the method by which it is produced appears capable of a more general application. This method is as follows:—

Iodide of æthylene, $C^4H^4I^2$ (a compound discovered by Faraday), is mixed in small portions with very dry acetate of silver. For 10 grms. of iodide 12 grms. (2 equivs.) of acetate of silver are taken. It is not advisable to operàte upon larger quantities. When the mixture is exactly made, it is put into a balloon, where a very brisk reaction soon commences; the mass grows yellow by the formation of iodide of silver, becomes heated, and evolves an abundance of gases, principally carbonic acid and olefiant gas, products of secondary reactions. As soon as the materials are cold, a fresh portion of the mixture is put into the same balloon, and this process is continued until 100 to 150 grms. of iodide of æthylene have been employed. After the last reaction the balloon contains a yellow mass of iodide of silver, impregnated with a liquid, which is distilled off by the naked fire, as it requires a pretty high temperature towards the end. An acid liquid is obtained, coloured brown by free iodine, and containing acetic acid, besides neutral products. This is submitted to fractional distillation. Ebullition commences at 248° F., but the temperature soon rises to 320° F., when the receiver is changed, and the portion passing between 320° and 392° F. is collected separately. The liquid obtained is still acid. It is distilled over litharge, and after several fractional distillations it passes almost entirely between 356° and 374° F. If it still contains a trace of iodine, it must be rectified over a small quantity of oxide of silver.

This product is diacetate of glycol, formed according to the following equation:—

$$C^4H^4I^2+2\left(\begin{array}{c}C^4H^3O^2\\Ag\end{array}O^2\right)=2AgI+\left.\begin{array}{c}C^4H^4\\C^4H^3O^2\\C^4H^3O^2\end{array}\right\}O^4.$$

Iodide of æthylene. Acetate of silver. Acetate of glycol.

The glycol itself, or diatomic alcohol, may be obtained by treating diacetate of glycol with caustic potash; it only differs from the diacetate in having the radical of acetic acid, $C^4H^3O^2$, replaced by hydrogen. Its atomic constitution is therefore represented by the formula—

$$\left.\begin{array}{c}C^4H^4\\H^2\end{array}\right\}O^4.$$

Diacetate of glycol is a perfectly colourless and neutral fluid, almost inodorous at ordinary temperatures, but evolving a slight acetic odour at a high temperature. It boils at 365° F., and distils without alteration. Its density is greater than that of water, to the bottom of which it sinks in large drops. A large quantity of water dissolves it, and it is soluble in alcohol. In the presence of water, bases decompose it into acetic acid and glycol. Its composition is expressed by the formula—

$$C^{12}H^{10}O^8=\left.\begin{array}{c}C^4H^4\\C^4H^3O^2\\C^4H^3O^2\end{array}\right\}O^4,$$

which has been established not only by analysis, but also by the determination of the density of its vapour.

The presence of 2 equivs. of acetic acid, or of the radical acetyle, was established by the following experiment. 1·298 grm. of acetate of glycol were saponified by an excess of hydrate of baryta, in a sealed tube, heated for two days in an oil-bath to 248°–266° F. The contents of the tube were then diluted with water, saturated with an excess of carbonic acid gas, and filtered. By precipitating the filtered liquid, which contained acetate of baryta, with sulphuric acid, 1·850 grm. of sulphate of baryta was obtained. Hence the acetate of glycol furnished 1·8 equiv. of acetic acid. It contains the elements of—

$$2C^4H^4O^4+C^4H^6O^4-4HO.$$

To isolate the glycol, 6·15 grms. of acetate of glycol were put into a balloon with 4·72 grms. of powdered hydrate of potash, previously heated to redness. An energetic reaction, accompanied by a slight evolution of heat, immediately took place. The next day the balloon was filled with a saline mass of acetate of potash. To complete the reaction, it was heated for two hours to about 354° F., and the temperature was then gradually raised to 482°–500° F. after providing the balloon with a small distilling tube. A perfectly transparent liquid distilled over drop by drop into a small receiving tube. By rectifying this liquid, and collecting separately the portion passing between 374° and 392° F., glycol was obtained.

In a pure state this constitutes a perfectly colourless and slightly viscous liquid, *endowed with a saccharine taste.* These properties resemble those of glycerine. It boils about 383° F., and distils without alteration. Its vapour is inflammable. It is soluble in all proportions in water and alcohol. Analysis:—

	Found.	Calculated ($C^4 H^6 O^4$).
C	38·7	38·7
H	9·9	9·6

Thus it only differs from ordinary alcohol in containing 2 equivs. more oxygen. From its mode of formation, it evidently contains the group $C^4 H^4$ (olefiant gas), and its constitution may be expressed by the formula—

$$\left.\begin{array}{r}C^4 H^4\\ H^2\end{array}\right\} O^4,$$

which represents a group of 2 molecules of water, $\left.\begin{array}{c}H^2\\ H^2\end{array}\right\} O^4$, in which H^2 is replaced by the diatomic radical, $C^4 H^4$. Olefiant gas is, in fact, a radical of this kind. It combines with 2 equivs. of chlorine, bromine and iodine, to form chlor-ætherene and its congeners*. It replaces 2 equivs. of hydrogen in the remarkable alkali acetylia, $\left\{\begin{array}{c}C^4 H^4\\ H\end{array}\right\} N$, discovered by M. Cloëz. In any case, highly interesting theoretical relations exist between water, alcohol, glycol and glycerine, as shown in the following table:—

Type, $\left\{\begin{array}{c}H\\ H\end{array}\right\} O^2$, Monoatomic alcohols.	Type, $\left\{\begin{array}{c}H^2\\ H^2\end{array}\right\} O^4$, Diatomic glycols.	Type, $\left\{\begin{array}{c}H^3\\ H^3\end{array}\right\} O^6$, Triatomic glycerines.
$\left.\begin{array}{r}C^4 H^5\\ H\end{array}\right\} O^2$, Ordinary alcohol.	$\left.\begin{array}{r}C^4 H^4\\ H^2\end{array}\right\} O^4$, Glycol.	$\left.\begin{array}{r}C^4 H^3\\ H^3\end{array}\right\} O^6$, Æthylic glycerine.
$\left.\begin{array}{r}C^6 H^7\\ H\end{array}\right\} O^2$, Propylic alcohol.	$\left.\begin{array}{r}C^6 H^6\\ H^2\end{array}\right\} O^4$, Propylic glycol†.	$\left.\begin{array}{r}C^6 H^5\\ H^3\end{array}\right\} O^6$, Glycerine.

The reaction which produces diacetate of glycol is more complex than is indicated in the equation already given. Carbonic acid and olefiant gas are evolved, and acetic acid and iodine are set free. But besides these, another secondary product is an oleaginous liquid which remains in the distillatory apparatus when the acetate of glycol has passed, and only distils at a temperature above 482° F. From an analysis, it appears to be an acetine of æthylic glycerine, $C^4H^6O^6$.

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* Iodide of æthylene may be regarded as the di-iodhydrine of glycol, $C^4 H^4 I^2 = C^4 H^6 O^4 + 2HI - 4HO$. The same relation exists between iodide of æthylene and glycol, as between iodide of æthyle, $C^4 H^5 I$, and alcohol, $C^4 H^6 O^2$. Each equivalent of iodine is replaced by the group HO^2.

† Bromide of propylene, $C^6 H^6 Br^2$, decomposes acetate of silver. This reaction will no doubt furnish propylic glycol, $C^6 H^8 O^4$.

Other salts of silver are decomposed with great facility by iodide of æthylene. Benzoate of silver furnished iodide of silver, free benzoic acid, and a neutral oleaginous compound, which is probably benzoate of glycol.—*Comptes Rendus*, July 28, 1856, p. 199.

On the Oxychlorides. *By* W. CASSELMANN.

The author has prepared some compounds with oxychloride of phosphorus, whilst endeavouring to obtain some new facts for the settlement of the question, whether the adoption of oxygenated radicals be admissible or not.

By heating oxychloride of phosphorus with various chlorides in sealed tubes, he prepared the following compounds:—

Chloride of Tin and Oxychloride of Phosphorus, $2SnCl^2 + PO^2Cl^3$, which has previously been described by the author.

Chloride of Aluminium and Oxychloride of Phosphorus, $Al^2Cl^3 + PO^2Cl^3$.—This compound has a peculiar odour; it fuses at 329° F., and solidifies on cooling in thin layers, in a decidedly crystalline form and colourless; in larger quantities it has the colour of chloride of aluminium. It boils at a heat below redness. Exposed to the air, it attracts water and deliquesces, but not so rapidly as the tin compound. It dissolves in water, with strong evolution of heat; the solution contains alumina, muriatic acid and phosphoric acid.

Chloride of Magnesium and Oxychloride of Phosphorus, $2MgCl + PO^2Cl^3$.—This compound is inodorous, and deliquesces rapidly when exposed to the air. By a large quantity of water it is decomposed, with a remarkably strong evolution of heat, and the chloride of magnesium dissolves more rapidly than the oxychloride of phosphorus, which is seen for some time swimming at the bottom of the vessel in drops. By a slight red heat it is decomposed into oxychloride of phosphorus, which distils over, and chloride of magnesium, which remains.

In the compounds of tin and aluminium the oxygen is certainly not combined with the metal, for when heated the compounds are completely volatilized without any residue of phosphates.

Oxychloride of phosphorus does not act upon chloride of copper.

Powdered perchloride of mercury, on the contrary, covers itself with clear colourless crystals, when it is kept near 212° F. for a considerable time with oxychloride of phosphorus in sealed tubes. The chlorides of potassium, sodium, and barium are converted into gelatinous masses, from which we may conclude that these chlorides also combine chemically with oxychloride of phosphorus.

With the metallic oxides, oxychloride of phosphorus does not behave like phosphoric acid, but becomes decomposed in such a manner that metallic chlorides and phosphates are produced. Hence the author concludes that oxychloride of phosphorus cannot be regarded as a phosphoric acid in which oxygen has been replaced by chlorine. On the other hand, in its property of entering into combination with the metallic chlorides, it agrees perfectly with the other electro-negative perchlorides (bichloride of sulphur and pentachloride of phosphorus). It possesses a particularly great similarity to the pentachloride of phosphorus.

The author has also ascertained, by the treatment of oxychloride of phosphorus with zinc in closed tubes, that in this case only oxide of zinc is formed and free phosphorus separated. From this he concludes that in oxychloride of phosphorus the phosphorus is to be regarded as electro-positive constituent, and not as a radical containing oxygen.

Consequently as regards the question of oxygenated radicals, the properties of oxychloride of phosphorus do not speak in favour of a constitution,—

$$PO^2, Cl^3,$$

according to which it would be a compound of a radical PO^2 with chlorine, but rather for a constitution which the author expresses by the formula—

$$P\left\{\begin{matrix}O^2\\ Cl^3,\end{matrix}\right.$$

which therefore only contains phosphorus as an electro-positive constituent.

The experiments which the author has made for the conversion of oxychloride of phosphorus, PO^2, Cl^3, into pentachloride, PCl^5, gave no results. He has therefore studied the relation of oxychloride of phosphorus, $PO^2 Cl^3$, to oxychloride of chrome, $CrO^2 Cl$. A portion of this substance, freed by repeated distillation from any intermixture of chlorine, was mixed with oxychloride of phosphorus; the mixture was distilled in tubes, to free it from any phosphoric acid that might be present, and then sealed up. Under these circumstances an action commences even at ordinary temperatures, resulting in the deposition of a black solid substance. The tubes were heated nearly to 212° F. in a box of Beindorf's apparatus surrounded with sand. The separation of the solid body constantly increased, until at last the whole mass was solid, and the vacant space above it appeared of an intense yellow colour.

The examination of the mass in the tube, on opening which a great quantity of chlorine without oxygen escaped, showed that the two bodies had acted upon each other in accordance with the following equation:—

$$5PO^2 Cl^3 + 12CrO^2 Cl = 18Cl + 5PO^5 + 3Cr^2 O^3 + 3Cr^2 Cl^3,$$

leaving out of consideration a small quantity of chromic acid which had been produced by moisture.

In this case also no pentachloride of phosphorus is produced. But it is remarkable that in this decomposition chlorine is expelled from the phosphorus compound by oxygen, and the presence of oxygenated radicals in the two oxychlorides cannot well be admitted.

For it is difficult to understand why the oxygen should quit the radical CrO^2, to enter into a new combination (phosphoric acid) as an electro-negative constituent. If, on the contrary, we regard the compounds as $P + \left\{\begin{matrix} O^2 \\ Cl^3 \end{matrix}\right\}$ and $Cr + \left\{\begin{matrix} O^2 \\ Cl \end{matrix}\right\}$, there are fewer difficulties in the explanation of this decomposition.

The author therefore concludes that neither oxychloride of phosphorus nor oxychloride of chrome contain oxygenated radicals, but that they are rather products of substitution of chlorine compounds in which a portion of chlorine is replaced by oxygen. With regard to the organic oxygenated radicals of monobasic acids, the author has commenced some experiments. Perchloride of benzoyle, $C^{14}H^5O^2Cl$, appears to enter into combination with chloride of aluminium.—Liebig's *Annalen*, xcviii. p. 213.

On the Nature of the Tannic Acids. By Prof. ROCHLEDER.

The author has been for some years investigating the so-called tannic acids. The analyses of these substances with material prepared at different times have given such concordant numbers, that the author considers he may depend on the correctness of the percentage compositions obtained. To get a clear insight into their constitution, the author availed himself of their behaviour to acids, by which some of the tannic acids are decomposed into two products, whilst others are not. Difficulties of many kinds present themselves in the investigation of this process, and it was desirable to discover another mode of decomposing these substances, for which purpose the action of the alkalies appeared deserving of study. In the presence of air, however, products of oxidation immediately result by the action of alkalies, and these render an investigation of the true products of decomposition quite impossible.

This is not the case when alkalies are allowed to act upon the tannic acid in the absence of oxygen. Hydrate of baryta is preferable to the other alkalies, as baryta is easily got rid of entirely, and determined with exactness. For treatment with baryta, the author employs a very simple apparatus, arranged for operating with exclusion of air.

Hydrogen gas is evolved in a vessel, and this after washing passes into a flask containing the tannic acid in concentrated solution. When the flask is quite filled with hydrogen gas, the solution of baryta is poured in through a funnel. The funnel has a long neck reaching to the bottom of the flask, and is closed at the top by a ground-glass rod. If the funnel be filled with solution of baryta with the glass rod inserted, and the latter be then loosened a little, the solution flows down to the tannic acid, without carrying with it any air-bubbles. A third tube leading into a tubulated receiver enables the water distilled off to be collected for examination; the tubulure is furnished with a tube drawn out into an open point, so that aqueous vapour and hydrogen gas may escape. The current of hydrogen gas may easily be rendered uniform, by pouring the acid into a funnel closed with a glass rod, on the side of which a small channel is cut, to allow the acid to flow down very slowly upon the zinc.

When the action of the baryta has continued long enough, the hydrogen gas is replaced by carbonic acid until all the baryta is converted into carbonate, or the solution may be decomposed by dilute sulphuric acid. In this way the products of decomposition are obtained without injurious subsidiary products, which are produced under other circumstances by the action of oxygen.

The method of decomposing the tannins and tannin-like bodies by sulphite of ammonia, employed by Knop with gallotannic acid, is not generally applicable, as most of these acids furnish amorphous products, which are not only very difficult of separation, but often cannot be exactly separated from each other.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xviii. p. 3.

Synthesis of the Carburets of Hydrogen. By M. BERTHELOT.

1. The action of a mixture of sulphuret of carbon and sulphuretted or phosphuretted hydrogen upon copper at a dull red heat, produces hydrogen, marsh gas, $C^2 H^4$, a considerable quantity of olefiant gas, $C^4 H^4$, and a trace of naphthaline.

The proportion of olefiant gas may be rendered more considerable by the action of a mixture of sulphuret of carbon, marsh gas, and carbonic oxide on iron. In these circumstances, the proportion of olefiant gas formed may be such that its carbon will be equal to one-sixteenth of the carbon of the sulphuret decomposed.

The marsh gas formed in these experiments could be isolated by the use of solvents. The olefiant gas was collected in bromine, and disengaged in a state of purity from the bromine compound by a process which will be presently indicated; this olefiant gas was afterwards converted into crystallized sulphovinate of baryta and characteristic benzoic æther.

Thus the synthesis of alcohol by means of the simple bodies of which it consists may be regarded as an accomplished fact, for sulphuret of carbon is obtained by the direct union of carbon and sulphur.

2. In the dry distillation of formiate of baryta, carburetted hydrogen gas, olefiant gas, $C^4 H^4$, and propylene, $C^6 H^6$, are formed. Hence it follows that these two carburets and the corresponding alcohols may be obtained by complete synthesis; for I have shown, on the one hand, that the formiates may be prepared by means of oxide of carbon, and on the other, that the preceding carburets may be converted into the corresponding alcohols by the intervention of sulphuric acid or of the hydracids*.

3. If carbonic oxide and purified marsh gas be passed together into a tube heated to dull redness, a small quantity of propylene,

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* Propylene combines directly with muriatic, hydrobromic and hydriodic acids, forming the corresponding æthers.

$C^6 H^6$, is obtained. Marsh gas alone does not furnish anything of the kind under the same conditions.

4. In the dry distillation of acetate of soda, olefiant gas, $C^4 H^4$ (in very small quantity), propylene, $C^6 H^6$, butylene, $C^8 H^8$, and a little amylene, $C^{10} H^{10}$, are formed. The carbon contained in these various carburets may rise to one-twentieth of the total carbon contained in the acetate. It will be observed that the acetates are prepared simply by means of the alcohol derived from the olefiant gas which is formed in the preceding reaction.

5. The various carburets just referred to were condensed in bromine, and studied separately after being disengaged in a pure state by the following process. The bromine compound is heated to about 482° F., in a hermetically-sealed tube, with copper, water and iodide of potassium. By this process, olefiant gas, propylene, &c., may easily be regenerated from their bromides. If the copper be omitted, the hydrurets of the carburets of hydrogen are obtained; thus the bromide of olefiant gas, $C^4 H^4 Br^2$, furnishes the carburet $C^4 H^6$, and the bromide of propylene, $C^6 H^6 Br^2$, gives the carburet $C^6 H^8$. This is a very general process of inverse substitution.

6. From the preceding facts, and the relations which exist between the carburets of hydrogen and the alcohols on the one hand, and the alcohols and the other organic compounds on the other, we may regard the complete synthesis of a great number of organic compounds as an accomplished fact.—*Comptes Rendus*, July 28, 1856, p. 236.

On Anisylic Alcohol. By S. Cannizaro *and* C. Bertagnini.

When oil of aniseed is boiled for an hour with about three times its volume of dilute nitric acid of 14° B., hydruret of anisyle is obtained. It forms a heavy oleaginous substance, which is washed with water and dilute solution of potash, and then distilled. The distillate is agitated with a hot solution of bisulphite of soda of 30°, and left standing after cooling, when the crystalline compound of hydruret of anisyle with the sulphite is washed with alcohol until it becomes white, and the solution of the compound is heated with a concentrated solution of carbonate of potash; the hydruret of anisyle separates in a stratum floating on the surface, which is drawn off and distilled.

If the hydruret of anisyle be then dissolved in an equal volume of alcohol and mixed with three times its volume of a solution of potash of 7° B., it is decomposed into anisic acid, which crystallizes, and anisylic alcohol, which remains in solution. The alcohol is distilled off on the water-bath, the residue diffused in water, and the anisylic alcohol extracted by means of æther, which furnishes it on evaporation in the form of a brown oil. If this oil be distilled, it passes over at 500° F. in the form of a colourless fluid, which soon crystallizes.

The body thus obtained is usually mixed with a little hydruret of anisyle, which remains on treatment with alkaline bisulphites. The pure anisylic alcohol distils without decomposition at 479° to 482° F., and fuses at 73° F., when it is anhydrous, but otherwise it crystallizes at a lower temperature in hard shining needles. It is heavier than water, and has a weak, spirituous, sweetish odour, and a burning taste, resembling that of oil of anise. It undergoes no change even by long exposure to the air at ordinary temperatures, but near its boiling-point it absorbs oxygen, and becomes converted into hydruret of anisyle.

Oxidizing substances convert it with great ease, first into hydruret of anisyle, and afterwards into anisic acid. Platinum-black converts it in a few days into anisic acid. Dilute nitric acid also has a similar action.

Anisylic alcohol dissolves various salts with the assistance of heat, such as benzoate, anisate and acetate of potash; on cooling, these salts crystallize from it. Salicine, phillyrine, and hippuric acid are also soluble in it. Potassium produces an evolution of hydrogen with anisylic alcohol, which becomes violent when assisted by heat. The alcoholate of potassium produced subsequently forms a butyraceous mass.

Sulphuric acid converts anisylic alcohol into a reddish resinous mass, even at a moderate heat. Phosphoric acid has the same action. Chloride of zinc also decomposes it, forming water, which is taken up by the chloride of zinc, and an oily supernatant stratum. Muriatic acid gas passed into anisylic alcohol, appears to form the chloride of the radical contained in it.

Hydruret of salicyle (salicylous acid, $C^{14} H^{6} O^{4}$), when treated in the cold with an aqueous or alcoholic solution of potash, undergoes no further change; and it is only when the solutions are so concentrated that the hydrate of potash melts, that salicylate of potash is formed. The alcohol corresponding with salicylic acid could not be obtained in this way.—Liebig's *Annalen*, xcviii. p. 188.

On the Nature of the Liquid secreted by the Abdominal Gland of the Insects of the Genus Carabus. *By* J. Pelouze.

Having observed that the liquid secreted by the *Carabi** presented an odour of butyric acid, the author examined this secretion to discover whether that acid really existed in it.

The liquid is secreted in a gland at the hinder portion of the abdomen, and is ejected when the insect is irritated. The most simple method of collecting it is to put the hinder extremity of a *Carabus* into the mouth of a test-tube, and irritate it by pricking its head. By repeating this process with several specimens of the *Carabus*, a sufficient quantity is obtained for examination. It is found to contain a considerable quantity of butyric acid, which is recognized,—

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* The species examined by the author are *C. niger* and *C. auratus*, the first of which is not found in this country, whilst the other is of rare occurrence here. His observations however will apply equally to the other species, several of which may be met with in abundance in fields and gardens.

1. By its characteristic odour, like that of rancid butter.

2. By its strongly reddening blue litmus.

3. By its possessing the property, when neutralized by alkalies, and especially by baryta-water, of leaving a solid residue, which exhibits a very marked gyratory movement on water.

4. The secretion of the *Carabi*, when mixed with alcohol and sulphuric acid, gives rise to a volatile inflammable liquid, which presents the pine-apple odour of butyric æther. The ætherification takes place at the ordinary temperature, as is also the case with ordinary butyric acid. These characters leave no doubt of the presence of butyric acid in the secretion, but the author could not obtain it in sufficient quantity for analysis.

It is remarkable that butyric acid, although it contains no nitrogen, is generally formed under the influence of animal matters. The excrements of carnivorous animals contain butyric acid, which has not been found in those of Herbivora. Putrefying animal matters furnish butyric acid. In presence of caseous matter, which contains so much nitrogen, sugar, gum, starch, &c. give such large quantities of butyric acid, that it is usually prepared with these substances.

All the parts of the intestinal canal of man, when well washed and brought in contact with a solution of sugar or starch-paste, give origin to butyric acid, the quantity of which varies in the different portions of the intestine. The same is the case with the intestine of the dog.

M. Pelouze also refers to the observation of Pfaff, that the odour diffused by the larvæ of *Chrysomela Populi* is due to the presence of hydruret of salicyle (salicylous acid), which it ejects when slightly pressed.—*Comptes Rendus*, July 21, 1856, p. 123.

On the Transformations undergone by Protochloride of Mercury under the Influence of Water, Alcohol and Heat. By M. Berthé.

From the author's experiments it appears,—

1. That under the influence of an elevation of temperature, and especially in the presence of alcohol and water, protochloride of mercury is decomposed, giving rise to a certain quantity of bichloride.

2. That Smithson's battery, in contact with calomel suspended in water, produces the same reaction, and that therefore whenever it is desired to deprive calomel of the bichloride which it may contain, or to prove the presence of this salt in it, the liquids (water, alcohol and æther) must be employed at the temperature of the atmosphere, and that before making use of Smithson's pile the limpidity of the liquid must be ascertained.

3. It may be deduced from these experiments, that if a continued temperature of 104° to 122° F. be sufficient to cause the partial conversion of protochloride of mercury into bichloride, it is scarcely doubtful that this must take place in the organism when it is exposed to a temperature near this in presence of alkaline chlorides. This

is a further proof of the opinion put forward by Mialhe as to the mode of action of this compound.—*Comptes Rendus,* July 21, 1856, p. 162.

Researches towards a History of Oil of Turpentine, and on a new Acid obtained by the Oxidation of the Hydrate of Turpentine.

By J. PERSONNE.

The acids hitherto obtained by the oxidation of turpentine have been produced by the action of nitric acid at different degrees of concentration. These are, the *terebic* or *terebilic acid,* $C^{14}H^{9}O^{7}$, HO, of Bromeis and Rabourdin; the *pyroterebilic acid,* derived from terebilic acid; and lastly, the terephthalic acid, $C^{16}H^{4}O^{6}$, 2HO, terebenzic acid, $C^{14}H^{6}O^{3}$, HO, and terechysic acid, $C^{6}H^{3}O^{4}$, HO, of A. Caillot.

On comparing the formulæ of these different acids with that of oil of turpentine, it is difficult to understand the reaction which has given origin to them. In fact, the oxidizing action of nitric acid is very complex, and the production of these different acids is always accompanied by that of several bodies produced simultaneously or by secondary actions. The employment of an oxidizing body of which the elements are very stable, led me to hope for a more simple and distinct reaction; potash, or what is better potash- or soda-lime, appeared to me to offer the best chance of success. By passing the vapour of hydrate of turpentine, $C^{20}H^{16}$, 4HO, over soda-lime heated to about 752° F., and treating the product with muriatic acid, *terebenthilic acid* was obtained.

This acid is solid, white, with a slight hircinic odour, and heavier than water; it melts at 194° F., and distils at 482° F. During its distillation a very small quantity appears to be decomposed; it is nearly insoluble in cold water, but more soluble in boiling water, from which it is deposited on cooling in the form of a white powder composed of little crystalline needles. It is very soluble in alcohol and æther. By sublimation it crystallizes in small laminæ, which appear to be oblique prisms. Its vapour is very acrid, and strongly irritates the nostrils. The composition of this acid is represented by $C^{16}H^{10}O^{4}$; this formula was determined by the analysis of the lime-salt, the silver-salt, the crystallized acid, and the distilled acid.

The analysis of the lime-salt gave CaO (average of ten analyses), 17·68 per cent.

The analysis of the silver-salt gave (average of three analyses) $C=38{\cdot}92$, $H=3{\cdot}70$ per cent.

The analysis of the same salt gave Ag (average of four determinations) $=43{\cdot}90$ per cent.

Calculation gives for the lime 17·83, and for the silver-salt

$$C=39{\cdot}18,\quad H=3{\cdot}67,\quad Ag=44{\cdot}08,$$

according to the formula $C^{16}H^{9}O^{3}$, HO.

Lime in combination with this acid forms a white salt crystallizing in small silky needles, which give it the aspect of sulphate of quinine, of which it possesses the lightness. The silver-salt is very soluble in boiling water, which allows it to crystallize in small quantity on cooling. Oxide of lead forms with it an uncrystallizable salt, which possesses when dry the aspect of fragments of gum-arabic. This acid ætherifies alcohol with the greatest facility, and yields an æther similar to the odoriferous æthers produced by the fatty volatile acids; its odour resembles that of the pear and pine-apple.

From its composition, *terebenthilic acid*, $C^{16}H^{10}O^4$, comes between caprylic acid, $C^{16}H^{16}O^4$, and toluic acid, $C^{16}H^8O^4$, from which it differs only by the amount of hydrogen.

The production of this acid by the action of soda-lime upon the hydrate of turpentine is accompanied by a pretty abundant evolution of gas, which I have ascertained to be a mixture of protocarbonated hydrogen and free hydrogen; this formation may be represented by the following equation:—

$$C^{20}H^{20}O^4 = C^{16}H^{16}O^4 + 4CH^2 + H^2.$$

Besides this gaseous mixture, a small quantity of liquid hydrate of turpentine (*terpinole*) is formed, but this product is only accidental. This formation of gaseous products would lead us to fear explosions, if, in order to operate more quickly and lose less of the product, we made use of a closed tube, as Delalande has done for campholic acid; it is better to use a tube open at one end, and consequently to operate at the ordinary pressure.—*Comptes Rendus*, September 8, 1856, p. 553.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Purification of Lead by Crystallization.

By WILLIAM BAKER, Lead Works, Sheffield[*].

THE following investigation and analyses were undertaken to find whether copper and iron could be separated from lead in a similar manner to silver in Pattinson's crystallization process.

The principles of the process are these. When lead containing a certain amount of silver is melted and allowed slowly to cool, a crystallization of pure lead obtains at a temperature at which an alloy of silver and lead still remains fluid. The crystals of pure lead which sink towards the bottom of the vessel may be removed by means of a perforated ladle.

In a battery of four pots, each containing about 6 tons of metal, samples were taken from each pot,—1st, when melted and skimmed; 2nd, from the crystals when about half the desired quantity had been ladled out; 3rd, from the fluid lead containing the alloy of silver and lead called the "bottoms."

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[*] Communicated by the Author.

The lead employed at the commencement was of very fair quality, as the following analyses of two samples show:—

In 100 *parts.*

	I.	II.
Silver	0·0046	0·0052
Copper	0·0066	0·0154
Iron	0·0065	0·0068
Sulphur	trace	trace

Annexed is a tabular view of the results obtained by analysis of the samples of lead taken as above described. It will at once be perceived that a similar law regulates the separation of copper as of silver from lead; that is to say, there is an alloy of copper and lead which remains fluid at a temperature at which crystals of pure lead are formed. Iron, it will be seen, cannot be removed by this method, but is chiefly separated by oxidation, and during the operation of skimming the surface of melted metal:—

In 100 *parts.*

	Silver.	Copper.	Iron.
Rich pot.			
Before crystallizing	0·0108	0·0344	0·0312
Crystals, 25 parts	0·0052	0·0152	0·0086
Fluid lead, 85 parts	0·0140	0·0476	0·0122
Second pot.			
Before crystallizing	0·0052	0·0154	0·0068
Crystals, 95 parts	0·0020	0·0066	0·0118
Fluid lead, 25 parts	0·0126	0·0286	0·0146
Third pot.			
Before crystallizing	0·0020	0·0102	0·0118
Crystals, 70 parts	0·0010	0·0038	0·0198
Fluid lead, 25 parts	0·0100	0·0240	0·0082
Fourth pot.			
Refined lead	0·0014	0·0054	0·0112

By the first crystallization silver is reduced from 0·0108 per cent. =3 oz. 10 dwts. 13 grs. per ton to 0·0052 per cent.=1 oz. 13 dwts. 23 grs. per ton in the crystals, and concentrated to 0·0140 per cent. =4 oz. 11 dwts. 11 grs. per ton in the fluid lead left in the pot.

Copper from 11 oz. 4 dwts. 16 grs. per ton is reduced to 4 oz. 19 dwts. 7 grs. in the crystals, and concentrated to 15 oz. 10 dwts. 23 grs. in the fluid lead.

In the second crystallization, the separation is still more apparent, as a larger proportion of crystals are removed than in the first. Ultimately the silver is reduced to only 9 dwts. 3 grs. per ton, and copper to 1 oz. 15 dwts. 6 grs. per ton in the refined lead.

It will be seen that the amount of foreign metals in the crystals should in each case correspond to that in the metal of the next pot before crystallization; and in most cases it is identical, in others sufficiently near to prove the truth of the analyses.

Although iron appears in the first crystallization to be removed in a similar manner, yet upon repeating the operation it does not diminish in quantity in the crystals, nor become concentrated in the fluid lead; but rather the minimum seems to be in the samples of lead taken before crystallization, that is, immediately after skimming. Contact with the iron vessels and ladles then supplies the increased per-centage in the crystals.

From these experiments it is clear that copper, when not contained in considerable quantities, may be separated from lead by a similar process to Pattinson's desilverizing process.

August 29, 1856.

On a Mode of giving a Metallic Surface to Horn.

By M. MEUNIER.

The articles made of horn are first prepared as usual, and then coated with chloride of zinc, either by immersion or with a brush. A yellow bronze colour is produced; chloride of copper gives a blackish-bronze, chromate of copper a brown-bronze, and chromate of zinc a green colour. Iodide of potassium, applied over any of the copper colours, renders them red. The objects soaked with the solutions of these salts are exposed to a temperature of 154° F., and rubbed after drying with a mass composed of 5 parts of mercury, 15 parts of tin, 3 parts of sulphur, and 5 parts of muriate of ammonia, in the preparation of which the mercury and tin are first combined into an amalgam, which is then powdered and mixed with the other substances. The objects are then heated in a flask in the sand-bath until the mercury is evaporated, and a yellow mosaic gold is obtained.—*Polyt. Centralblatt,* 1856, p. 574.

On the Solubility of the Colouring Matter of Madder in Water, between 212° *and* 482° F. *By* MM. E. M. PLESSY *and* P. SCHÜTZENBERGER.

Madder, and even madder-flowers, contain the colouring principle mixed with too much foreign matter, to allow a single treatment with water in a closed vessel to give very distinct results. Instead of operating on madder, the authors have therefore employed the concentrated methylic extract, which is the most conveniently prepared according to a process indicated by Gerber and Dollfus.

10 grms. of this extract, previously triturated, were put with 100 grms. of distilled water into a copper tube closed by a screw-stopper. The apparatus was placed in an oil-bath, and heated for fifteen minutes to 482° F. On cooling, the liquid was entirely filled with crystalline needles of a fine pale red. These crystals were easily separated by decantation from the undissolved excess of extract, which remained in a hard lump at the bottom of the tube. The weight of the crystals was only 1·63 grm.; and the residue, treated in the same way with 100 grms. of water, furnished a fresh quantity of crystals. In nine operations the colouring matter was exhausted, and the water no longer acquired colour. Nearly a fourth of the extract employed was obtained in crystals; the residue

consisted of a brown resin, the alcoholic solution of which no longer acquired a violet colour with ammonia.

The colouring matter was in a state of great purity; it was crystallized a second time in water of 482° F., to get rid of the little resin which it might still retain. Its physical properties and analysis show it to be identical with the sublimed alizarine of Robiquet and Collin. Its dyeing power is also identical, and much greater than that of madder or madder-flowers; the authors value it at 80 times that of madder-flowers, and 40 times that of madder.

The solubility of alizarine in water at different temperatures is as follows:—

At 212° F.	100 grms. of water dissolve	0·034
302° F.	... ...	0·035
392° F.	... ...	0·82
437° F.	... ...	1·70
482° F.	... ...	3·16

Comptes Rendus, July 21, 1856, p. 167.

PROCEEDINGS OF SOCIETIES.

Royal Society.

"Chemical Examination of Burmese Naphtha, or Rangoon Tar." By Warren De la Rue, Ph.D., F.R.S., and Hugo Müller, Ph.D.

In several localities of the kingdom of Burmah, there emanates from the soil in considerable quantity a peculiar oleaginous substance, which is employed for a variety of purposes, but chiefly as a lamp-fuel and as an unguent, by the natives, and exported in moderate quantities under the name of Burmese naphtha, or Rangoon tar.

It is obtained by sinking wells of about 60 feet in depth, in which the liquid is collected by the miner as it oozes from the soil.

At the common temperature this substance has the consistence of goose-fat; it is lighter than water, has usually a greenish-brown colour, and possesses a slight odour, peculiar, but not disagreeable. It consists almost entirely of volatile constituents.

Burmese naphtha has already attracted the attention of other chemists; at present we refrain from entering into a discussion of their results, since it is our intention to give a full history of this remarkable natural product when, after the completion of our experiments, we shall have the honour of submitting to the Royal Society a detailed account of our investigation. The object of the present communication is to trace a mere outline of the results at which we have arrived up to this moment.

The circumstances under which petroleum—for this is the collective term which comprehends a great variety of oily emanations similar to Burmese naphtha—occurs in nature, all tend to prove that these substances are the products of a slow destructive distillation of the residuary matter of a primeval creation: this being admitted, the idea naturally suggested itself of examining this substance in comparison with the products of artificial destructive distillation.

With this view, one of us* was induced to procure, through the intervention of a friend, several tons of Rangoon tar, which was carefully collected at the source, and transmitted to Europe in well-secured vessels. Our experience in the course of this inquiry, has shown that this quantity, large as it may appear, was by no means too ample a supply. Burmese naphtha contains indeed so great a variety of substances, and some of them in so exceedingly minute a proportion, that even the large amount of material at our disposal was insufficient for the complete examination of several constituents, the presence of which we had succeeded in establishing beyond a doubt. As an example, we may state that Burmese naphtha contains small quantities of organic bases, the study of which we were compelled to postpone to a later period, when an additional quantity of material, which is now on its way to Europe, will have come to hand.

We have already mentioned that Rangoon tar is almost entirely volatile, and preliminary experiments proved to us that the distillation could be effected most conveniently, and with less danger of obtaining products of decomposition, in a current of steam; first of a temperature of 100° C. (212° F.), and subsequently of steam superheated by passing, before it entered the still, through a system of pipes the temperature of which could be regulated. Treated in this way, it furnishes 96 per cent. of volatile products, fluid and solid.

Steam of 100° C. (212° F.) carries over 11 per cent. of a volatile oil perfectly free from solid hydrocarbons, which at that temperature are entirely retained in the distillatory apparatus. Between the temperatures of 110° and 145° C. (230°–293° F.), 10 per cent. of a further distillate is obtained, which is almost free from solid hydrocarbons. The temperature may be raised to 160° C. (320° F.) without materially augmenting this per-centage; but on gradually increasing the temperature of the steam to the fusion-point of lead, the operation yields 20 additional per cent. of distillate, which retains its fluidity at 0° C. (32° F.), notwithstanding the presence in it of an appreciable quantity of solid matter. At this stage of the process the products of distillation begin to solidify on cooling, and about 31 per cent. of a crystalline material is obtained sufficiently consistent to be submitted to pressure. After this the consistence of the products of distillation begins to diminish; and whilst the temperature of the steam is considerably raised, 21 per cent. of a mixture of solids and liquids distil, the latter predominating especially as the operation proceeds.

In the last stage of the process the distillate completely changes its character, becoming very dark in colour, of a pitch-like consistence, and exhibiting scarcely an indication of the presence of crystalline matter. When this product, which amounts to about 3 per cent., has passed over, there remains in the still a coke-like mass, which contains a small quantity of earthy impurities.

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* Warren De la Rue.

Although there is a considerable difference between the specific gravities of the first and last fractions of the distillates, all the products of distillation, like the original oil, are lighter than water, and could be separated therefore by means of the well-known apparatus (called a Florentine flask) employed in the distillation of essential oils.

By exposing the distillates obtained beyond the temperature of 145° C. (293° F.) to a freezing mixture, nearly all the crystalline matter solidified, and became removeable by means of filtration and pressure. It was thus ascertained that Rangoon tar contains from 10 to 11 per cent. of solid constituents (paraffine).

Solid Constituents.

The solid product, when removed from the fluid hydrocarbons, still retains a portion of the latter with much obstinacy; in order to purify the solid, it has to be subjected to the action of boiling concentrated sulphuric acid, and to be subsequently washed, first with an alkaline solution, then with water. On redistillation, the paraffine is obtained quite white, but even now it still retains some fluid hydrocarbons which have resisted the action of the sulphuric acid; the greater part can be removed by pressure between folds of cloth in a powerful hydraulic press and subsequent exposure for some months to the air, in which the fluids gradually disperse. By fractional crystallization from hot alcohol, we have been enabled to separate the solid product into at least two distinct compounds, which appear to have the same per-centage composition, agreeing either with $C_n H_n$ or $C_n H_{n+1}$, but which differ from each other in their physical properties. By the action first of sulphuric acid saturated with anhydrous acid, then with *anhydrous* sulphuric acid itself, we believe that we shall obtain compounds which will enable us to determine a rational formula for each of these interesting bodies.

Liquid Constituents.

In order to purify the liquid constituents of Burmese naphtha, they were, after the separation of the solid portion from such as contained any, twice redistilled in a current of steam, first of 100° C. (212° F.), and subsequently of superheated steam, the temperature of which was gradually raised. In the redistillation, however, steam of only 100° C. (212° F.) was found to carry over fluids which boiled at a temperature as high as 300° C. (572° F.).

A further separation of the various products was effected by repeated fractional distillations; but no absolutely constant boiling-points could be obtained, notwithstanding the great number of distillations and the large quantity of material at command. It is true that considerable portions of distillates could be collected between certain ranges of temperature, tending to indicate a constant boiling-point; nevertheless it soon became evident that distillation alone could not effect the separation of the various constituents, and that recourse must be had to other processes. The employment of concentrated sulphuric acid first suggested itself, and by its means a whole group of hydrocarbons could be removed from the distillates, the residue consisting of hydrocarbons, on which it had no action. This was an important step; but recourse was subsequently had, with even more success, to the action of strong nitric or a mixture of nitric and sulphuric acids, by which means a series of nitro-compounds were obtained, which presented the advantage of being more easily studied than the sulpho-acids. The nitric-acid method, which has already been described at some length*, promises to be of general applicability in the separation of complex mixtures of hydrocarbons, and has, in the hands of Mr. C. Greville Williams†, been lately employed with advantage in the investigation of "Some of the products of the distillation of Boghead Coal at low temperatures."

Hydrocarbons separable by Sulphuric Acid and Nitric Acid.

The proportion of hydrocarbons removeable from the various distillates by means of concentrated sulphuric acid, nitric acid, or a mixture of both acids, is in most cases small when compared with the part not acted upon; it increases generally, however, with the boiling-point of the fluid, varying from less than one-tenth to nearly one-third part of the original compound-hydrocarbon. The nitro-compounds obtained by means of strong nitric acid are fluids at the lower end of the series, whilst with hydrocarbons boiling above 200° C. (392° F.) they are of a resinous consistence; they frequently retain with obstinacy a portion of the not-acted-upon hydrocarbons, and more especially if the experiment be conducted upon a small scale; nitro-compounds are sometimes obtained which float upon water, in consequence of this retention of the lighter hydrocarbons.

In submitting the hydrocarbons to the action of the acids, we have invariably selected fluids which from their boiling-points appeared to be within certain limits homogeneous; but notwithstanding every possible care in this selection, we have always obtained more than one sulpho-acid and more than one nitro-compound, as the case might be, and we have experienced very considerable difficulties in the separation of the mixed products. In the case of nitro-compounds, advantage has sometimes been taken of their convertibility by a mixture of sulphuric and nitric acids into di- and tri-nitro-compounds, which admitted of fractional crystallization from various media. We have been thus enabled to isolate the following compounds, the analysis and properties of which place their existence beyond doubt, namely,—

Nitrobenzole,
Dinitrotoluole,
Trinitroxylole,
Sulphocumolate of barium;

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* In the specification of a patent granted to Warren De La Rue, Dec. 23, 1854, and entitled "Improvements in treating products arising from the distillation of a certain Tar or Naphtha, to render the same suitable for dissolving or removing Fatty or Resinous Substances."

† Proceedings of the Royal Society, vol. viii. p. 119.

and therefore it is evident that the Burmese naphtha products contain the corresponding hydrocarbons, namely,—

Benzole	$C_{12}H_6$
Toluole	$C_{14}H_8$
Xylole	$C_{16}H_{10}$
Cumole	$C_{18}H_{12}$

But we have found that the foregoing are by no means the only hydrocarbons separated by sulphuric acid and nitric acid, and we hope to establish the existence of other series containing terms isomeric with, but differing in properties from, benzole and its homologues; we have, moreover, good reason to suspect the presence of other compounds even less linked with the benzole series.

Action of Reducing Agents on the Nitro-compounds.

In order to throw further light on the constitution of the hydrocarbons in Burmese naphtha, removeable by the before-named acids, we have submitted the several nitro-compounds to the action of reducing agents. As was to be expected, our nitrobenzole yielded an abundant supply of aniline when distilled with acetic acid and iron turnings, thus confirming the existence of benzole beyond all possible doubt. In a similar manner the presence of toluole was further established by the preparation of nitrotoluole and toluidine. Béchamp's method was, however, not equally applicable in all cases, so that Zinin's original sulphide of ammonium process was resorted to; by its means we have obtained several new bases, and among them one crystallizing beautifully in long needles, having the appearance and colour of alizarine. Some time must however elapse before the great number of new bodies can be fully studied.

Hydrocarbons not acted upon by Sulphuric and Nitric Acids.

The hydrocarbons which resist the action of monohydrated sulphuric and nitric acids form, as has been before stated, by far the larger portion of the distillates obtained from Burmese naphtha. When purified by washing from adhering acid, by fractional distillation, and finally by rectification in a current of dry hydrogen gas over the liquid alloy of potassium and sodium, they are obtained almost inodorous and perfectly colourless. Thus purified, they are very fluid, and retain their fluidity even in the intense cold produced by a mixture of solid carbonic acid and ether. No absolute fixity of boiling-point could be obtained in any of the products; nevertheless a much greater constancy in this respect was observed than with the hydrocarbons before treatment with strong acids. The lowest boiling-point obtained was 50° C. (122° F.); the highest, being far beyond the range of the mercurial thermometer, was not ascertained. The specific heat of the vapour of all this series of hydrocarbons was ascertained to be very small, a fact which we believe accounts in some measure for the difficulties we experienced in the fractional distillations. For the purpose of analysis, we have contented ourselves with selecting such products as boiled within the same 5° C. (9° F.)

the whole of the aluminium, but usually only one-fourth to one-third, and in the most favourable case two-thirds. As a good deal of sodium was always burnt in his experiments, the author thinks that its quantity might be reduced.

The advantages of this process are, that earthen crucibles may be employed, as in the reduction of other metals, that the mass is readily fusible without eating through the crucible, and that the aluminium is obtained free from silicium. The reduction does not take place nearly so well with chloride of sodium alone.

It would be a great advantage to prepare fluoride of aluminium directly from the cryolite, and thus increase the amount of aluminium from 13 to 32 per cent. None of the author's experiments led to this result. Cryolite is not decomposed by sulphate of alumina. When heated with 3 equivs. of sulphuric acid with the view of decomposing only the 3 equivs. of fluoride of sodium, a good deal of fluoride of aluminium is also decomposed. By heating it with one-fourth or one-third of its weight of muriate of ammonia in a platinum crucible, one-third of the fluoride of sodium may certainly be converted into chloride of sodium, and after this has been washed out the amount of aluminium increased from 13 to 16 per cent.; but this is too tedious, and the advantage is too small.

Small grains of aluminium may be fused in a porcelain crucible under a layer of chloride of magnesium, which is more easily prepared than chloride of aluminium and sodium, and is not decomposed by aluminium.

No aluminium was reduced by the current of a single electrical couple from a solution of cryolite in soda.—Liebig's *Annalen*, xcix. August 1856, p. 255.

On Collodion. *By* L. HOFMANN.

The author has occupied himself with the preparation of collodion for photographic purposes, and recommends the following process, which may also be rendered applicable in surgery by additions. The best addition is castor oil, to deprive the collodion of the property of contracting so strongly and becoming cracked.

1 part of loose, clean cotton-wool is immersed for a quarter of an hour in a mixture of 20 parts of dry nitrate of potash, and 30 parts of English sulphuric acid, in a suitable glass vessel, capable of being closely covered with a glass plate. During this time it is once strongly stirred. The mixture is then poured into a pail of pure water, and well washed, and this operation must be repeated until the last traces of salt and acids are removed. The xyloidine obtained is then put into a linen cloth, pressed sharply, and teased out before drying, so as to remove all knots. The drying is effected upon a common stove in a suitable sieve.

Schacht has already recommended the same proportions, but has not prescribed the employment of the dried salt, and he has also confined the time of action to 4–5 minutes. Xyloidine thus prepared did not dissolve so readily and completely in the mixture of æther and alcohol, and the preparation in course of time lost the property of dissolving easily. 6 parts of xyloidine, obtained by the above process, were dissolved by shaking in a mixture of 120 parts of æther and 8 parts of the most highly rectified alcohol, and 3 parts of castor oil were added to the solution.—*Archiv der Pharm.*, cxxxviii. p. 146.

On the Products of the Volcanoes of Southern Italy.
By C. SAINTE-CLAIRE DEVILLE.

The author has investigated some products of the volcanic mountains of Italy. The following investigations of the gaseous products were made by him in common with Leblanc and Lewy:—

1. Gas which was collected in May, June, September, and October 1855, at various points of the stream of lava from the eruption of Vesuvius, on May 1, 1855.

The analyses of this gas showed that the gas which accompanies those fumaroles which the author calls dry fumaroles, and which only carries with it anhydrous alkaline chlorides and small quantities of sulphates, is nothing but a stream of air either unaltered or containing less oxygen; thus 20·1, 20·6 per cent. of oxygen were found in it. The same is the case with the gas loaded with vapours of muriate of ammonia, which was expelled from the lower parts of the lava in October.

2. Gas collected in September from the fumaroles on the small plain in the centre of the upper crater of Vesuvius.

It gave aqueous vapour of the temperature of 140° to 174° F., mixed with a little vapour of sulphur and sulphuretted hydrogen. In one sample of this gas 3·51, in another 9·26 per cent. of carbonic acid were found. The remainder was only air, from which nearly all oxygen was extracted.

3. Gas collected in September and October from those fumaroles on the summits of Vesuvius and Etna which throw up a mixture of aqueous vapour, muriatic acid, and sulphurous acid at high temperatures (194°, 257°, and 356° F.). This again is nothing but air deprived of some oxygen.

4. Gas collected in September 1855, on the upper border of the cone of eruption of Etna (1852). This upper margin in June still possessed an abundance of fumaroles of sulphuretted hydrogen of 182° F.; in September they only emitted aqueous vapour of 142° F., which was perfectly neutral, and the vapour was only accompanied by air.

The constitution of these gases, which escape from the summits of Vesuvius and Etna, is such as we might have expected; air is always intermixed with the gases, and the emanations of carbonic acid, sulphur, sulphuretted hydrogen, muriatic acid, and sulphurous acid are products such as the cleft crater must furnish in the same way as a cracked chimney over a fire.

5. Gas collected on the 5th and 22nd of October in the Lago di Naftia or Lac de Palici, in Sicily.

This gas consisted of—

	Oct. 5.	Oct. 22.
Carbonic acid	..	5·00
Oxygen	17·36	15·77
Nitrogen	82·64	79·23

The composition of this gas therefore varies with time. In none of the gases could a combustible gas be detected.

The second part of the work which the author has undertaken relates to the solid products of the eruption of 1855. This is not yet completed, but the following statements may be made already.

Two kinds of lava flowed out in this eruption. The one which made its appearance last is dark, as it were furnished with a glassy coating, and has no action upon the magnet, whilst the other kind is gray, much more crystalline, and strongly magnetic. Both contain nearly the same amount of iron, so that the iron is not contained in the same form in the lavas.

The one contains 1·4, the other 2·2 per cent. of phosphoric acid. Both contain some chlorine, a portion of which is as it were intermixed in the form of soluble chloride, whilst another portion is not washed out with water, but only obtained by the decomposition of the mineral with bisulphate of potash. The author lays particular stress upon the presence of phosphoric acid, which is now generally recognized, partly by himself and partly by other observers, in all volcanic masses, and also upon the presence of chlorine, which constitutes about $\frac{3}{1000}$dths of the lava examined. He also found chlorine in the rocks of Puracé, in an amphigenous stratum of the Somma, and in a slag-like stratum of the same mountain.

The author then endeavoured to determine the nature of the white mineral, which occurs in small, roundish, apparently dodecahedral masses in the lavas of Vesuvius, and which appears to replace felspar. He has not however as yet succeeded perfectly. At all events the felspar of the lavas of Vesuvius appears to be an amphigenous one, and is distinguished from that of the Somma by its only containing traces of soda; whilst in the felspar of the lava of 1855 the oxygen of the soda is in the proportion to that of the potash as 2·09 : 1; this proportion in the mineral of Fossogrande is 8·21 : 1, and in the amphigenous perfect crystals, which were thrown out of the volcano on the 22nd of June, 1·67 : 1, according to Damour.—*Comptes Rendus*, xlii. p. 1167.

Employment of Carbazotic Acid (Welter's *Bitter*) *in Medicine.*

By MM. CALVERT *and* MOFFAT.

According to the author's observations, carbazotic acid (picric acid) cures violent diarrhœas in doses of 0·05 to 0·10 grm. three times a day. It is found in the urine of persons who have taken it. It is remarkable that the patients (whether men or animals) who take this acid acquire a yellow skin, as if they had the jaundice.—*Comptes Rendus*, xliii. p. 104.

On the Alkaline Oxalates. By MM. SOUCHAY *and* E. LENSSEN.

The authors have investigated the series of compounds of soda with oxalic acid, $C^4H^6, 2HO$, which they regard as bibasic, and have prepared the following compounds:—

Neutral Oxalate of Soda, $2NaO, C^4O^6$ (*air-dried*).—This salt is not very easily prepared. Cold solutions of carbonate of soda and oxalic acid readily furnish mixtures of bicarbonate of soda and oxalate of soda. To obtain it pure, the solution of carbonate of soda must be added to the hot solution of oxalic acid until the fluid only retains a slight acid reaction. The salt being difficult of solution, is partially thrown down, even at a boiling heat, in the form of a white sandy powder.

1 part of the salt dissolves in 31·1 parts of water at 60° F., and in 15·8 parts of boiling water. The solution changes red litmus to blue, and does not give a brown colour to turmeric. Alcohol throws down the salt as a soft voluminous precipitate. The composition is as already stated by Graham. It appears that this salt does not exist with water of crystallization.

Acid Oxalate of Soda, $NaO, HO + C^4O^6 + 2HO$, forms small hard crystals, permanent in the air, dissolves in 60·3 parts of water at 60° F., and in 4·7 parts of boiling water. It strongly reddens blue litmus. The solution, prepared hot, readily remains supersaturated on cooling.

This salt is easily obtained by dividing a solution of oxalic acid into two equal parts, exactly saturating the one with carbonate of soda and adding the other. The salt loses no water over sulphuric acid; at 212° F. it loses 13·84 per cent., or 2 equivs. The salt, dried at 212° F., is decomposed at 320° F., losing hydrated oxalic acid (not water, as Graham stated).

Tetraoxalate of Soda does not appear to exist; if oxalic acid and soda be brought together in the proportions corresponding with this salt, the binoxalate and free oxalic acid are obtained. Neither do the salts which contain both soda and ammonia, or potash and ammonia with the formula C^4O^6, the neutral salts of the bibasic acids with two kinds of bases, appear to exist; in experiments on their production, mixtures of salts were obtained.

The normal Oxalate of Baryta, $BaO, HO, C^4O^6 + 2HO$, dissolves, when freshly precipitated, in 2590 parts of cold, and 2500 parts of hot water. At 212° F. it loses 1 equiv. of water, and becomes BaO, BaO, C^4H^6, HO. This salt is also produced, as Wicke first discovered, when a solution of 2 parts of oxalic acid is gradually added to a concentrated cold solution of 25 parts of crystallized chloride of barium. This salt loses no more water at 212° F.; at 302° F. it becomes anhydrous.

Acid Oxalate of Baryta, $BaO, HO, C^4O^6 + 2HO$, is produced, in contradiction to Graham's statements, when oxalate of baryta is dissolved in hot concentrated oxalic acid, or when 1 equiv. of chloride of barium ($BaCl + 2HO = 122$) is dissolved in water, and this solution is mixed with that of 2 equivs. of crystallized oxalic acid

(126). The acid oxalate of baryta separates after some time in fine, delicate, shining needles, which are washed with a little cold water. As Bérard has correctly stated, the salt contains 2 equivs. of water of crystallization. Of this it loses 1 equiv. at 212° F., and has then the composition $BaO, HO, C^4 H^6 + HO$, as Wicke found. The 1 equiv. of water must also evidently escape *in vacuo*, as Clapton found the same constitution as Wicke for the salt dried *in vacuo*. The second equivalent of water of crystallization only goes off at 257° F.; at 284° F. oxalic acid escapes. The salt is difficult of solution in cold water. 1 part requires 392 parts of water at 62°·6 F. for its solution. This solution has a strong acid reaction. When treated with hot water, it is gradually decomposed; the crystals break up, with formation of neutral baryta-salt. It is insoluble in alcohol. The aqueous solution is precipitated on the addition of alcohol, and it is neutral oxalate of baryta that is precipitated.

Oxalate of Magnesia, $MgO, HO, C^4 O^6 + 4HO$, is obtained as a white sandy powder when carbonate of magnesia is added to oxalic acid. When prepared by the mutual decomposition of oxalate of potash and a soluble salt of magnesia, it retains potash. The salt only loses 1·51 per cent. of water at 212° F., as was already found by Graham. At 302° F. the salt becomes anhydrous, but at the same time partial decomposition takes place. The salt acquires a brown colour. If oxalate of magnesia be put into hot muriatic acid, of spec. grav. 1·12, as long as any of it is dissolved, oxalic acid separates in needles on cooling; all the magnesia remains dissolved. Salts of magnesia, mixed with acetic acid, are precipitated by oxalate of ammonia, and indeed very quickly. Oxalate of magnesia is thrown down, but this always contains small quantities of ammoniacal salts.

Oxalate of Potash and Magnesia, $KO, MgO, C^4 O^6 + 6HO$, is obtained when freshly precipitated oxalate of magnesia is added to the boiling solution of neutral oxalate of potash, until it is no longer dissolved by long boiling. The double salt is afterwards deposited from the filtrate in slightly transparent crystalline crusts. At 212° F. it loses 4 equivs. of water, or 18·64 per cent.

A corresponding *double salt of soda* does not appear to exist.

Oxalate of Ammonia and Magnesia.—If solutions of magnesia-salts and oxalate of ammonia be brought together, oxalate of magnesia is precipitated, always containing some of the double salt. A dilute solution of chloride of magnesium, mixed with oxalate of ammonia and some caustic ammonia, furnishes, after long standing, crystalline crusts of oxalates of ammonia and magnesia. They consist of compounds of the double salt $MgO, NH^4 O, C^4 O^6$ with the salt $(NH^4 O)^2, C^4 O^6$, in various, but equivalent proportions. All these salts do not separate for a considerable time; they are firmly deposited upon the walls of the vessel. The authors have prepared salts belonging here, of the following compositions:—

A. $2(MgO, NH^4 O, C^4 O^6) + 5(NH^4 O, NH^4 O, C^4 O^6) + 10HO.$

B. $5(MgO, NH^4 O, C^4 O^6) + 4(NH^4 O, NH^4 O, C^4 O^6) + 24HO.$

C. $MgO, NH^4 O, C^4 O^6 + 2(NH^4 O, NH^4 O, C^4 O^6) + 8HO.$

The last of these salts is always obtained when freshly precipitated oxalate of magnesia is added in small portions to a boiling concentrated solution of neutral oxalate of ammonia until no more of it is dissolved even by long boiling. It is filtered hot, and the filtrate is left to cool quietly. Verrucose crystals separate in hard crusts. They are of an enamel-white colour, slightly translucent and efflorescent in the air. At 212° F. the salt loses 13·30 per cent., or 6 equivs. of water. At 248° F. a quantity of water goes off corresponding with 7 equivs. At 284° F. the salt begins to decompose, becoming slightly brownish.

D. Oxalate of ammonia and magnesia, of the formula $MgO, NH^4O, C^4O^6 + 3(NH^4O, NH^4O, C^4O^6) + 8HO$, is obtained from the mother-liquor of the preceding salt, when it is mixed with a little water and ammonia, and left standing in the cold for weeks; it forms milk-white crusts, which dissolve in water with partial decomposition. At 212° F. it loses 12·15 per cent., or 8 equivs. of water. —Liebig's *Annalen*, xcix. p. 31.

Upon Cyanide of Æthyle and a new Formation of Æthylamine.
By Dr. Emil Meyer.

The author has submitted the various methods of preparing æthylamine to a comparative examination, after the completion of which he has come to the conclusion, that the method described by Hofmann, according to which it is prepared from iodide of æthyle and ammonia, is the best and most certain. Considerable quantities of iodide of æthyle are certainly requisite; but if this be prepared according to Dünhaupt's method, its preparation presents no difficulties.

The author regards Strecker's method, in which it is prepared from æthaminosulphate of ammonia, as unadvisable, as also that of Gössmann (from sulphite of aldehyde-ammonia), and that of Berthelot (from æthylosulphate of lime and an alcoholic solution of ammonia at 482° F.); that of Wurtz (from cyanic acid) is better.

The author has also made some observations upon cyanide of æthyle. In the attempt to prepare this body from iodide of æthyle and cyanide of silver, by heating them to 212° F. in a sealed tube, he obtained in a short time iodide of silver and a thick oil, whilst the iodide of æthyle disappeared. This oil consists of a compound of cyanide of æthyle with cyanide of silver and separated iodide of silver, from which however the cyanide of æthyle cannot be obtained pure, because this compound does not allow the escape of the cyanide of æthyle at 212° F., and at a higher temperature furnishes products of its decomposition.

Instead of iodide of æthyle and cyanide of silver, the author then heated a mixture of these bodies with water to 212° F. in sealed tubes. But by this means also he obtained no pure cyanide of æthyle, but a crystallized compound of

Cyanide of Silver with Cyanide of Æthyle, $AgCy + C^4H^5, Cy$.— This is obtained when the product of the heating in sealed tubes is repeatedly extracted with water, and the crystals obtained are collected. It is quickly dried between bibulous paper, as it soon becomes black in the air. The crystals are quadratic prisms, which appear beautifully coloured in polarized light. They fuse at 176° to 194° F. in closed tubes, are but slightly soluble in æther and alcohol, and are apparently decomposed thereby.

If the cyanide of silver and æthyle be distilled with potash, a distillate is obtained which smells strongly of cyanide of æthyle. If muriatic acid be added to it, the odour of cyanide of æthyle immediately disappears, and the residue contains two different bases in the form of muriates.

One of these is certainly æthylamine, which is therefore formed in this new way. The other appears to be a salt in which cyanide of æthyle may be considered as base, of the formula $C^6 H^5 N, HCl$. The author has not been able to overcome the difficulties presented by a complete separation of these bodies, and the discovery of their properties and composition.—*Journ. für Prakt. Chem.*, lxviii. p. 279.

Contributions towards the knowledge of the Lichens.

By Dr. T. Gerding.

By means of æther, the author has extracted a new body from *Parmelia physodes*; to this he gives the name of *physodine.* From the following description, it appears that this body belongs to the series of lichenic acids investigated by Held, Rochleder, Knop, and Schnedermann.

When sufficiently purified by solution in alcohol, this body forms a loosely coherent white mass, which when magnified 190 diameters appears as an aggregation of distinct, acicular, four-sided, truncated prisms; they begin to swell up towards their fusing-point (257° F.), and become converted into a deep rose-red body, nearly resembling cochineal powder in colour.

When the physodine is pure, it is insoluble in æther and ordinary alcohol, but soluble in boiling absolute alcohol; with water it behaves like a resin. Concentrated sulphuric acid dissolves this body at first with a violet colour, which afterwards passes to a deep rose-red or nearly a wine-red; so that this reagent, by extracting water, appears to produce the same red body which results from the employment of the above temperature in the dry way. By diluting this red solution of physodine in sulphuric acid, flakes of a bluish-violet colour are thrown down; these, when held up against the light, appear almost purple.

If the alcoholic solution of physodine be placed under a bell-glass, and exposed to the action of the ammonia evaporating from a cup filled with liquid ammonia, it acquires a beautiful yellow colour exactly like chrome-yellow; but with a slight access of air the colour passes in time to brownish-red.

The substance dissolves readily in caustic ammonia with the assistance of heat, and acquires a yellow colour, but the solution is very soon rendered reddish by the access of air, or rather by its oxygen. In a solution of potash of spec. grav. 1·26, the body is dissolved with a yellow colour still more rapidly, and instantaneously with the assistance of heat; the colour gradually passes to reddish by exposure to the air. When the solutions in potash and ammonia are neutralized by acids, pale yellow flakes are precipitated from the former, and reddish ones from the latter solution.

A solution of neutral carbonate of ammonia takes up but little physodine at ordinary temperatures, but dissolves it completely at a boiling heat. Carbonate of potash dissolves it with the aid of heat, more readily than carbonate of ammonia. No precipitate is produced in its alcoholic solution by an alcoholic solution of chloride of barium; but in a solution of physodine in potash, a dilute solution of chloride of barium causes a dingy yellow precipitate, whilst the supernatant fluid is of a wine-red colour. An alcoholic solution of acetate of lead produces a pale yellow precipitate, readily soluble in solution of potash, in an alcoholic solution of the body; an alcoholic solution of nitrate of silver causes a brownish-red precipitate, and a similar solution of sulphate of copper a pale green precipitate, which would lead to the formula $C^{20} H^{11} O^{15}$. The red body into which physodine is converted by heat, or by solution in sulphuric acid, is called *physodeine* by the author. It appears to be produced from the former by abstraction of water, and to have the constitution $C^{20} H^{9} O^{13}$. Analyses gave—

	Physodine dried at 212° F.	Physodeine.
C	49·68	51·08
H	4·62	4·00
O	45·80	44·92

Archiv der Pharm., cxxxvii. p. 1.

Advantageous Process for the Preparation of Lithia from Lepidolite.

By KARL VON HAUER.

Finely pounded lepidolite was well mixed with about half its weight of sulphate of lime, and exposed for two hours in a Hessian crucible to a red heat. On cooling, the mass, which was firmly caked together, but not fused, was lixiviated with hot water, and the solution separated from the insoluble residue by decantation. The solution contained nearly the whole of the potash, lithia, and manganese contained in the lepidolite, converted into sulphates by the sulphate of lime. The solution also contained a small quantity of alumina, and the proportion of sulphate of lime soluble in water.

The solution was evaporated to as small a volume as possible, as sulphate of lithia is very soluble in water. By this means a considerable portion of the much less soluble sulphate of potash crystallized out, as did also nearly all the sulphate of lime. The filtered fluid was mixed with ammonia, a little sulphuret of ammonium, and oxalate of ammonia. The precipitate thus produced, consisting of alumina, sulphuret of manganese and oxalate of lime, was separated, and all the lithia was then thrown down as carbonate, by means of carbonate of ammonia assisted by heat, and washed with cold water. To purify it completely from potash, it is well to repeat the last operation once more, by dissolving the carbonate of lithia in an acid, and precipitating it again by carbonate of ammonia.—*Journ. für Prakt. Chem.*, lxviii. p. 310.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of Hæmatosine and Albumen for Technical Purposes. By J. Pillans.

To obtain the hæmatosine, the author first subjects the blood to a treatment, by which it is separated into a clot and serum. From the clot the hæmatosine is obtained, and the serum is operated upon for albumen.

First Operation.—The blood, whilst still warm, and if possible just as taken from the animal, is collected in flat basins each capable of containing 8 to 10 litres. When these vessels are circular, with a flat bottom and perpendicular sides, which is the best form, they must be about 14 inches in diameter and 4 inches in depth. They may however be made smaller, especially for sheep's blood. They are furnished with two opposite handles attached to the outside.

When these vessels are nearly filled with blood, they are left standing for two to six hours according to the time of the year; in warm weather less time is required than in cold. The consistency of the blood, however, which varies essentially even in animals of the same species, also has an influence on the length of time for which it is necessary to leave it in repose. As a general rule, the blood should not be stirred until it is entirely coagulated, and shows a tendency to deposit the serum.

Second Operation.—The filter has the same form as the above, but a rather greater diameter. Its bottom and walls are pierced with numerous small apertures of 2½ lines in diameter; two handles are attached to it at the level of the bottom. When the blood has stood the requisite time in the collecting vessels, it is put into the filter in the form of a clot, without previously pouring off the serum, which is then got rid of by the further treatment.

Instead of the filter, an apparatus of the same form and diameter may be employed, but with the bottom and sides in separate pieces. The bottom is pierced with holes, and the walls consist of a ring of wood or metal. When the blood-clot is to be transferred from the collecting vessel, the bottom is laid upon the opening of the latter, which is then turned upside down; the rim is then attached to the bottom, and the basin is removed.

Third Operation.—The blood-clot lying on the filter is cut up small by means of a peculiar many-bladed knife. The serum still retained in the clot then begins to run away. At first it contains so much hæmatosine that it must be put to one side, so that it shall not contaminate that which flows subsequently. As soon as the serum flows away without colour, the filter with the clot is removed, and placed upon another vessel of the same form, but of rather larger size (the deposit-vessel), so as to allow the clear serum running through the filter to collect in it.

In the middle of the bottom of the deposit-vessel there is a hole of about an inch in diameter, which is closed with a stopper of cork or vulcanized india-rubber. Through the stopper a tube passes, of sufficient width to allow the fluid to run off, and projecting about 2 inches above and below the bottom of the vessel. This tube must fit exactly, but be capable of slipping through the stopper. The upper mouth of the tube must be closed as long as the serum is flowing, so as to prevent any of this from being lost, and frequently it is as well to have several such apertures in the bottom of the vessel.

In this vessel the serum is allowed to filter until nothing more runs away from the blood-clot. According to the time of the year, and other circumstances, from ten to twenty hours are required for this purpose. When all has run away, the filter is removed from the deposit-vessel, the serum is mixed with that which was collected before the cutting up of the clot, and the whole is left standing until it becomes clear, for which from twelve to twenty-four hours are required according to the temperature. The filter is placed in another flat vessel, in which a little more serum is collected, the clot being left to dry in the air until there is danger of the occurrence of decomposition. The clot is then removed, to be treated as hereafter described.

Fourth Operation.—The clear serum in the deposit-vessel is decanted or allowed to run off by opening the tubes, so as to leave only the deposit at the bottom, which is added to the coloured serum first collected from the divided clot.

By these operations three different products are obtained from the blood:—

1. The clot in a nearly dry state, containing the hæmatosine, a little serum, and nearly all the fibrine.
2. Serum much coloured by hæmatosine.
3. Clear serum.

These products were further treated in the following manner:—The clot may be treated in two ways. It is either cut up by a many-bladed knife into small pieces, and these put into a drying chamber with a good draft upon wooden trays or wire sieves, or the clot is pressed between rollers or in a press. Both the fluid and the solid mass obtained by the latter process, the latter consisting principally of fibrine, are dried. The temperature must be kept below that at which hæmatosine coagulates, so that it may be soluble in water. This is between 96° and 109° F.

The second portion of the blood, the strongly coloured serum, is then mixed with the fluid obtained by pressure in the preceding operation, and evaporated. When this portion of the blood, which the author also calls hæmatosine, is dry, it may be ground to powder; in which condition it is more or less adapted for various purposes, as for instance for the dyeing of Turkey-red and sugar refining.

The third portion of the blood or the clear serum is put into shallow saucers, in which it forms a thin stratum, and introduced into a drying chamber of the above temperature. When it is quite dry, it is taken out and pounded, when it can be used as albumen, especially in stuff-printing, to fix ultramarine-blue and other colours, or to clear certain fluids instead of white of egg.

Very different materials may be used for making the apparatus; for instance, glass, gutta percha, vulcanized india-rubber, zinc, enamelled iron, &c., but tin and tinned vessels must be avoided because they discolour the serum. It is advantageous to rub the vessels before using them with oil or some fatty substance.—Dingler's *Polytechnisches Journal*, cxl. p. 298.

On Rinmann's *Green.* *By* Prof. R. WAGNER.

Under the name of Rinmann's green (cobalt-green) is known a colour obtained in the latter part of the last century by Rinmann, a Swede, by the calcination of a mixture of oxide of zinc and protoxide of cobalt. The high price of the materials may be the principal reason why this colour has not come into general use. But since zinc-white has become a regular and cheap article of commerce, and protoxide of cobalt has also been brought into commerce at a low price and in a tolerably pure state, the conditions for the manufacture of cobalt-green have become more favourable than formerly; and the author has made experiments upon its preparation, of which the following are the results.

In the first place it is necessary to prepare a protoxide of cobalt as free as possible from foreign metals. For this purpose oxide of cobalt, such as is furnished by the Saxon blue manufactories, is employed; this is dissolved in 3 parts of concentrated muriatic acid, the solution is evaporated to dryness, the residue dissolved in 6 parts of water, and sulphuretted hydrogen gas is passed through the fluid as long as a precipitate is formed. The fluid filtered from the precipitated metallic sulphurets is again evaporated to dryness, and the residue is dissolved in so much water that the solution shall weigh 10 parts. A litre of the solution does not contain much less than 100 grms. of protoxide of cobalt, and 100 cub. centims. therefore contain 10 grms. This fluid is drawn off for use.

If this solution be precipitated with carbonate of soda, and the hydrated protocarbonate of cobalt produced be mixed whilst still moist after washing with oxide of zinc, a reddish-violet paste is obtained, which, when dried and long calcined, forms a green mass, the colour of which is intense in proportion to the quantity of solution of cobalt employed. Cobalt-green may be regarded as a mixture of zincate of protoxide of cobalt (corresponding to the aluminate of protoxide of cobalt in cobalt-ultramarine, or Thenard's blue) with oxide of zinc. From well-calcined cobalt-green ammonia first of all extracts oxide of zinc, and afterwards the cobalt compound dissolves. Glass fluxes, as might be expected, are coloured blue by cobalt-green. If the cobalt solution be employed in such quantity that there may be more than 1 equiv. of protoxide of cobalt to 1 equiv. of oxide of zinc, a dingy green or even black mass is obtained after calcination; this is probably a mixture of the compound ZnO, CoO with an excess of protoxide of cobalt. The most agreeable greens are obtained when 1 to 1½ part of protoxide of cobalt is employed with 9 to 10 parts of oxide of zinc. The tints however never equal those of a bright copper-green, nor even those of the green ultramarine.

The Belgian chemist Louyet has ascertained that an addition of phosphoric or arsenic acid in the preparation of cobalt-ultramarine increases the beauty of the colour. If the addition of acids favours the combination of protoxide of cobalt with alumina, the presence of these acids must also have a favourable influence on the production of cobalt-green. If the above-mentioned solution of cobalt be precipitated by phosphate of soda or arseniate of potash, the phosphate or arseniate of protoxide of cobalt thus obtained possesses the property of communicating the green colour to oxide of zinc, even at a lower temperature than ordinary protoxide of cobalt. The protoxide of cobalt is also broken up and rendered more productive by these two acids, and the green colour is rendered purer and more brilliant. Alkaline arsenites behave like the arseniates and phosphates. If the mixed mass before calcination be mixed with a small quantity of arsenious acid and then calcined, an extraordinarily brilliant green mass is obtained, to which the arsenious acid, which is partially volatilized, has given a loose spongy consistence, in consequence of which it is easily triturated.

Experiments with silicic and boracic acids and oxide of antimony did not give favourable results.—*Kunst- und Gewerbeblatt für Bayern*, 1856, p. 83.

On Caseine Cement. *By* Prof. R. Wagner.

If caseine, precipitated from milk by means of acetic acid, be dissolved in bicarbonate of potash or soda, a fluid is obtained which possesses adhesive properties in a high degree, and was recommended twenty years ago by Braconnot as a cement. The author, by employing various other alkaline solvents for the solution of the washed and pressed caseine, obtained cements which possess valuable, or at all events noticeable properties.

By dissolving caseine in a cold saturated solution of borax, a clear fluid of a thickish consistence is obtained, which is remarkable for its high adhesive power, in which it far exceeds gum-arabic. This fluid gives a slightly shining, varnish-like coating to paper which is covered with it; and the paper thus coated may be employed with much advantage for tickets, which only need to be moistened to make them adhere firmly. It may also take the place of glue in many cases. Experiments in glueing wood with it gave the most favourable results. The fluid may also be employed in place of albumen in stuff-printing, in the manufacture of artificial meerschaum, to give lustre and consistence to silk fabrics, in the preparation of English plaster, artificial flowers, &c. Woollen and cotton stuffs, soaked with the solution and then dried, may be tanned with tannic acid or acetate of alumina, and thus converted into waterproof stuffs. A solution of caseine in soluble glass is to be recommended as a cement for porcelain and glass. Mixed with calcined magnesia, this fluid might perhaps be suited for the preparation of artificial meerschaum. By dissolving caseine in phosphate of soda ($PO^5, 2NaO, HO$), a fluid is obtained, which may also be employed as a cement and paste, but which is far inferior to the borax solution. It contains but little caseine. A solution of caseine in bicarbonate of soda may probably be employed for the sizing of papier maché.—*Polytechn. Centralbl.*, 1856, p. 958.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 12, 1856. (The Lord Wrottesley, President, in the Chair.)

"Letter from Dr. W. Bird Herapath to Professor Stokes, 'On the Detection of Strychnine by the formation of Iodostrychnine.'"

Bristol, June 7, 1856.

My dear Sir,—Will you do me the favour to announce to the Royal Society, that I have been engaged during some time past in the application of my discovery of the optical properties of iodostrychnine to the detection of this alkaloid in medico-legal inquiries? I find it is perfectly possible to recognize the 10,000th part of a grain of strychnine in pure solutions by this method, even when experimenting on very minute quantities. In one experiment I took $\frac{1}{1000}$th of a grain only, and having produced ten crystals of nearly equal size, of course each one, possessing distinct and decided optical properties, could not represent *more* than the $\frac{1}{10000}$th part of a grain; in fact, it really represents much less, inasmuch as one portion of the strychnine is converted by substitution into a soluble hydriodate, and of course remains dissolved in the liquid.

In order to operate in this experiment, it is merely necessary to use diluted spirit of wine, about in the proportions of one part of spirit to three of water, as the solvent medium, and to employ the smallest possible quantity of the tincture of iodine as the reagent, and after applying heat for a short time, to set in repose. On spontaneous evaporation or cooling, the optical crystals deposit themselves, and may be recognized by the polarizing microscope, according to the description given of this substance in a former notice to the Society in June last.

I remain, &c.,
W. Bird Herapath.

"Researches on the Action of Sulphuric Acid upon the Amides and Nitriles, with Remarks on the Conjugate Sulpho-acids." By George B. Buckton, Esq., F.L.S., F.C.S., and A. W. Hofmann, Ph.D., F.R.S.

Since we had the honour of addressing the Royal Society upon the subject of the behaviour of acetamide and acetonitrile towards sulphuric acid, we have completed our experiments upon the amides and nitriles, and extended our researches to other groups of bodies. The results of these additional inquiries we now beg to present in the form of a second short summary, the analytical details and the more extended description of the new compounds being given in the complete memoir, which, at the same time, we have the honour of submitting to the Society.

Before proceeding, however, to give an account of our new compounds, it may be desirable to state that several considerations, suggested by the progress of our inquiry, have induced us finally to adopt the name of Disulphometholic acid instead of the provisional term Tetrasulphomethylic acid under which we have described, in our first communication, the new acid generated by the action of sulphuric acid upon acetamide and acetonitrile.

ETHYLE-SERIES.

Action of Sulphuric Acid upon Propionitrile.

Considerable difficulty is experienced in preparing this nitrile in a state of purity. It was finally obtained by acting upon propionamide with anhydrous phosphoric acid.

When three parts by measure of the nitrile are cautiously mixed with two parts of fuming sulphuric acid, and heat is applied, the liquids enter into a sort of ebullition, carbonic acid being copiously evolved; at the same time a portion of propionic acid passes into the receiver, the amount of which may be lessened by raising the temperature only gradually.

At the close of the operation a tenacious mass is found in the retort, which, when dissolved in water and neutralized with carbonate of barium, furnishes two rather soluble but readily crystallizable salts, very difficult to separate one from the other. Their isolation may be conveniently effected, by converting them into the corresponding ammoniacal compounds, by precipitating their solution with carbonate of ammonium.

The filtrate yields two substances, one of which crystallizes, while the other is quite uncrystallizable.

The latter substance, when long digested with carbonate of barium, produces crystals of a barium-salt whose analysis gives numbers leading to the formula

$$C_6(H_4Ba_2)S_2O_{10}.$$

This substance is obviously sulphopropionate of barium, the compound next in series to the sulphacetate discovered by M. Melsens.

It is generally deposited from its solution in fine silky crystals, which arrange themselves in spherical groups. They are very stable, and bear a high temperature without decomposition.

The salt associated with the uncrystallizable sulphopropionate of ammonium crystallizes with ease, either in rectangular prisms or in octohedra. Similarly converted into a barium-compound, it was found by analysis to contain at 100° C.,

$$C_4(H_4Ba_2)S_4O_{12}+2HO.$$

It forms regular six-sided plates, which are moderately soluble in water, but insoluble in alcohol and in ether. It loses two equivalents of water of crystallization between 100° and 170°, but a few degrees above this temperature it is decomposed with blackening, yielding water, sulphurous acid, volatile organic products, and sulphate of barium.

We designate this salt as disulphetholate of barium.

Disulphetholic acid is prepared by precipitating a solution of the barium-salt with sulphuric acid, the excess of which is again removed by digestion with oxide of lead, and subsequent treatment with sulphuretted hydrogen. It is a crystalline and stable compound, very acid to the taste, and very deliquescent. With oxide of lead, or with carbonate of silver, it readily forms the respective salts, both of which are crystalline.

After what has been said with reference to the action of sulphuric acid upon acetamide, it is scarcely necessary to remark that the sulphopropionates and disulphetholates may be prepared with equal, or even greater facility from propionamide. Care, however, should be taken to use the amide in a perfectly dry state, which prevents in great measure the formation of free propionic acid.

PROPYLE-SERIES.

Action of Sulphuric Acid upon Butyramide.

Equal parts by volume of melted butyramide and Nordhausen sulphuric acid evolve much heat when mixed together. In the reaction two acids are eliminated, showing that the series bears a strict analogy with the deportment exhibited by the preceding group.

As the ammonia-salts of these acids are wholly uncrystallizable, their separation is almost impossible. The barium-compounds also are scarcely to be obtained of a definite form, so that it is a matter of great difficulty to procure salts of sufficient purity for exact estimation. Recourse was had to fractional precipitation by alcohol.

The first salt which was deposited formed minute grains, which adhered strongly to the sides of the glass vessel containing the solution. It gave a percentage of barium which unmistakeably indicated the formula

$$C_8(H_6Ba_2)S_2O_{10},$$

which is that of sulphobutyrate of barium.

This substance in its reactions closely resembles (with the exception of its greater solubility in water) the corresponding body of the ethyle-series. It burns like tinder, with evolution of sulphurous acid, and leaves a residue of sulphite and sulphate of barium. The aqueous solution presents a gummy mass on evaporation.

A further addition of alcohol to the mother-liquor of the sulphobutyrate of barium throws down a flocculent precipitate, which is very soluble in water. It was purified by repeated and partial precipitation with alcohol. This substance, when dried at a temperature of 165° C., furnished upon analysis numbers agreeing with the expression

$$C_6\,(H_6\,Ba_2)\,S_4\,O_{12},$$

which is that of disulphopropiolate of barium.

PHENYLE-SERIES.

Action of Sulphuric Acid upon Benzonitrile.

From the results obtained in the study of the methyle-, ethyle-, and propyle-series, we may fairly infer that all the homologues of other groups will exhibit a similar deportment.

It appeared, however, desirable to extend our researches to a class of bodies which are analogous (not homologous) to the preceding series.

Sulphuric acid appears to act with much less energy upon benzonitrile or cyanide of phenyle than upon the foregoing nitriles. No evolution of gas is observed until the mixture of the two substances is strongly heated, and then so much sulphurous acid is formed from charring of the cyanide that its presence is almost entirely masked.

The digestion was continued for two hours, after which the dark residue was treated in the usual manner for the soluble barium-salts. That first obtained consisted of sulphobenzoate of barium. For identification, both the neutral and acid compounds were prepared, the respective formulæ of which,

$$C_{14}\,(H_4\,Ba_2)\,S_2\,O_{10},$$

and

$$C_{14}\,(H_5\,Ba)\,S_2\,O_{10},$$

were corroborated by analysis.

An examination of the mother-liquor proved, as we had anticipated, the presence of a more soluble salt. By rapid evaporation it appears as an amorphous mass, but a drop allowed to dry spontaneously on the stage plate of the microscope exhibits it in the form of minute shuttle-shaped crystals.

The formula of this body, deduced from a sulphur- and barium-determination, is

$$C_{12}\,(H_4\,Ba_2)\,S_4\,O_{12},$$

which characterizes it as disulphobenzolate of barium.

The question naturally suggested itself, whether the same acid could not be prepared directly from the hydrocarbon benzole.

Mitscherlich has already described an acid (the sulphobenzolic) in which one equivalent of that hydrocarbon is associated with one equivalent of bibasic sulphuric acid. We have proved by experiment that sulphobenzolic acid takes up the elements of an additional equivalent when it is submitted to the prolonged action of Nordhausen sulphuric acid, and that, in fact, the union of these two bodies presents the most ready method of procuring disulphobenzolic acid in a state of purity.

The preceding researches establish in two different groups of bodies the existence of a series of bibasic acids containing four equivalents of sulphur, and which, irrespectively of any special view regarding their molecular arrangement, may be represented as formed by the association of the hydrocarbon (corresponding to marsh-gas) of the various groups with four equivalents of anhydrous sulphuric acid,—

Disulphometholic acid	$C_2\,H_4\,4SO_3$.
Disulphetholic acid	$C_4\,H_6\,4SO_3$.
Disulphopropiolic acid	$C_6\,H_8\,4SO_3$.
Disulphobenzolic acid	$C_{12}\,H_6\,4SO_3$.

An acid of analogous composition exists in the naphthaline-series, disulphonaphtholic acid, $C_{20}\,H_8\,4SO_3$, which was discovered by Berzelius, and subsequently studied by Laurent. Many of these substances may be actually obtained directly from the hydrocarbons by the action of sulphuric acid.

On the other hand, chemists are well acquainted with the deportment of olefiant gas under the influence of anhydrous sulphuric acid. The crystalline compound discovered by Magnus, and described by him under the name of sulphate of carbyle, whatever its constitution may be, can be considered as a direct combination of olefiant gas, with four equivalents of anhydrous sulphuric acid,—

Sulphate of carbyle ...... $C_4\,H_4\,4SO_3$.

It can scarcely be doubted that all the other hydrocarbons, $C_{n2}\,H_{n2}$, propylene, butylene, amylene, &c., will furnish homologous substances.

Sulphate of carbyle, when submitted to the action of water, assimilates two equivalents, and is converted into a bibasic acid (ethionic), $C_4\,H_4\,4SO_3 + 2HO = C_4\,H_6\,O_2\,4SO_3$, which accordingly may be viewed as an association of alcohol with four equivalents of anhydrous sulphuric acid. Terms analogous to ethionic acid are sure to be found when the study of the homologues of sulphate of carbyle shall be taken up by chemists.

The production of disulpho-compounds of perfectly similar composition, from substances belonging to such different groups of bodies, as the hydrocarbons homologous and analogous to marsh-gas, ethylene and alcohol, suggested the possibility that the substances in question might be but individual examples illustrating a far more general mode of formation. It became, in fact, probable that all organic bodies capable of uniting with the elements of two equivalents of anhydrous sulphuric acid might, under favourable circumstances, be induced to assimilate two additional equivalents of anhydrous sulphuric acid, and thus furnish other terms belonging to the class of disulpho-compounds.

The only additional class of compounds to which we have as yet successfully extended our labours, is the group of organic bases.

Action of Sulphuric Acid upon Aniline.

The first product which sulphuric acid forms with aniline is simply the sulphate of the base.

A further addition of acid, assisted by heat, dissolves the sulphate, and after a sufficiently long digestion, the whole is converted into sulphanilic acid. If too high a temperature be employed, the acid becomes very dark in colour; and indeed there is a limit beyond which carbon is rapidly deposited, accompanied by the evolution of abundance of sulphuric acid.

The process of converting sulphanilic acid into the disulpho-compound is rather tedious. It may, however, be effected without fail, by treating for several hours the perfectly dry crystalline acid, mixed with strong Nordhausen acid, to the consistence of a paste. The heat should not exceed that at which sulphurous acid just commences to be evolved. We employed an air-bath heated from 160° to 170° C., and the digestion was continued until a portion removed by a glass rod showed no trace of crystallization when cooled or moistened with water.

Treatment with carbonate of barium yielded in this manner a very soluble salt, which furnished a brittle gum when evaporated. The new substance was precipitated from its solution by alcohol and dried at 200° C. A determination of the barium and the sulphur led to the expression

$$C_{12}\,(H_5\,Ba_2)\,N\,S_4\,O_{12},$$

which is the formula of disulphanilate of barium.

This salt is readily attacked by concentrated nitric acid with oxidation of the sulphur. It blackens when strongly heated on platinum foil, and yields sulphurous acid without inflaming, a deportment in which it differs from sulphanilate of barium, which burns with a bright flame. When heated in close vessels it forms a crystalline sublimate, which consists of sulphite of aniline.

Disulphanilic acid is prepared by decomposing the lead-salt with hydrosulphuric acid. It is very soluble in water, and crystallizes with difficulty. It may be precipitated from a strong aqueous solution by alcohol in the form of white grains. The precipitation is assisted by the addition of a little ether. It has a very rough and acid taste.

We have also prepared the silver-salt by saturating the acid with carbonate of silver. The most ready method of obtaining it in a solid state is by precipitation with alcohol and ether. The aqueous solution, by concentration, deposits a black powder which makes it very difficult to obtain the crystals colourless.

The formula of disulphanilate of silver is

$$C_{12}\,(H_5\,Ag_2)\,N\,S_4\,O_{12}.$$

The potassa-salt is crystalline. It forms small grains or minute needles, which are insoluble in alcohol, The researches detailed in the preceding paragraphs may serve to characterize more fully a class of compounds of which only a few terms, isolated and scattered in widely different groups, had been previously observed. The only disulpho-acids hitherto known, are Berzelius's and Laurent's disulphonaphthalic acid, Magnus's ethionic (disulphethylic) acid, and lastly, dithiobenzic acid, recently discovered by M. Kilkenkamp. To these we now add five new acids, belonging to several of the most important series of compounds:—

Disulphometholic acid	$C_2H_4S_4O_{12}$.
Disulphetholic acid	$C_4H_6S_4O_{12}$.
Disulphopropiolic acid	$C_6H_8S_4O_{12}$.
Disulphobenzolic acid	$C_{12}H_6S_4O_{12}$.
Disulphanilic acid	$C_{12}H_7NS_4O_{12}$.

Our experiments point out, moreover, the universal occurrence, and the general mode of formation of these substances. All organic molecules, particularly in the nascent state, appear to be capable of assimilating the elements of either two or four equivalents of anhydrous acid.

The formation of the two groups of acids which are thus produced presents a great analogy with the production of the nitro-substitutes generated under the influence of nitric acid. All these compounds are generated with the elimination of water. In the action of nitric and sulphuric acid upon benzole, for instance, we have,

$$\underbrace{C_{12}H_6}_{\text{Benzole.}}+HNO_6=\underbrace{C_{12}H_5NO_4}_{\text{Nitrobenzole.}}+2HO$$

$$\underbrace{C_{12}H_6}_{\text{Benzole.}}+2HNO_6=\underbrace{C_{12}H_4N_2O_8}_{\text{Dinitrobenzole.}}+4HO$$

$$\underbrace{C_{12}H_6}_{\text{Benzole.}}+H_2S_2O_8=\underbrace{C_{12}H_6S_2O_6}_{\text{Sulphobenzolic acid.}}+2HO$$

$$\underbrace{C_{12}H_6}_{\text{Benzole.}}+2H_2S_2O_8=\underbrace{C_{12}H_6S_4O_{12}}_{\text{Disulphobenzolic acid.}}+4HO$$

The analogy of these reactions is obvious.

The action of nitric acid upon organic bodies is by no means limited to the production of nitro-compounds corresponding to nitrobenzole and dinitrobenzole; frequently additional substitutes are formed with elimination of six, eight, and in a few isolated cases, even of ten equivalents of water. It is possible that analogous sulpho-compounds may exist. Hitherto, however, no substances have been observed in which the assimilation of sulphuric acid has gone further than in the disulpho-acids.

THE CHEMICAL GAZETTE.

No. CCCXXXVII.—November 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Nitrous Acid upon Naphthylamine.

By L. Chiozza.

R. Ganahl has made some experiments with naphthylamine. If nitrous vapours be passed into a mixture of naphthylamine with a little water, an evolution of gas is immediately perceptible, which arises from a decomposition of the naphthylamine; the mass acquires a blue colour, and then becomes gradually purple by the formation of the product of oxidation characterized by Piria as *Naphthameine*. By a longer continued action of the nitrous acid, a resinous residue is obtained, together with a small quantity of a crystalline powder, which readily dissolves in alcohol with a citron-yellow colour.

The latter substance is obtained more easily and in greater abundance when nitrate of naphthylamine moistened with water is treated in the same way. In this case the decomposition goes on more rapidly, and nitrogen gas is evolved, without the appearance of the blue colour; the mass gradually becomes yellowish-brown, and if the action of the nitrous acid be stopped as soon as the mass has changed its appearance, and the mixture be then heated to boiling, a brisk evolution of gas takes place, which still continues several hours after cooling. After some time the greater part of the nitrate of naphthylamine is converted into a brown powder, which may be separated from the acid fluid by filtration; after washing with water, this powder is dissolved in boiling alcohol, and again precipitated by the addition of water. In this way orange-yellow flakes are obtained, and after repeated recrystallization of these from alcohol, reddish-brown needles, which appear under the microscope as transparent yellow laminæ.

The substance thus obtained is soluble in æther and in ammonia. It has all the properties of an acid. Its ammoniacal salt separates by the spontaneous evaporation of its solution in the form of yellowish laminæ, which dissolve readily in boiling water. Solutions of baryta- and lead-salts produce citron-yellow precipitates in it; potash, soda, and nitrate of silver form orange-yellow precipitates.

The new substance possesses a very distinct colouring power; it colours the skin and tissues yellow; this property, and still more the slight solubility of its potash-salt, might lead to its being confounded with picric acid. But the numbers obtained by the analysis of this substance do not agree with the composition of picric acid. Another property which distinguishes this substance from picric acid is, that the former does not explode when heated; it may be sublimed in a glass tube without explosion.

The analysis gave the following numbers with substance twice (I.) and three times (II.) recrystallized:—

	I.	II.	III.
C	53·11	52·80	
H	3·46	3·26	
N	..	..	12·50

These results lead to the formula $C^9H^3NO^4$, which must be doubled, for the analysis of the silver-salt leads to the formula $C^{18}H^6N^2O^8$. This silver-salt gave 33·33 per cent. of metal; calculated, 33·53 per cent. The formula $C^{18}H^6N^2O^8$ requires—

		Found.
C	52·4	52·80
H	2·9	3·26
N	13·6	12·5
O	31·0	31·4

Thus the only considerable difference between the calculation and experiment is in the nitrogen. I am aware that this formula must be confirmed by other experiments and the investigation of the products of substitution of this body, upon which I hope soon to be able to give some further communications.—Liebig's *Annalen*, August 1856, p. 240.

On the Albuminoid Substances, and their Conversion into Urea.

By MM. BÉCHAMP *and* PICARD.

M. Béchamp has shown that urea is derived from albumen or analogous azotized products, and that albumen may be directly converted into urea by a slow combustion, effected by means of a solution of permanganate of potash, at a temperature of about 176° F. This slow combustion is effected in the organism by the act of respiration.

M. Picard shows the presence of urea in the blood and its diffusion in the organism. Prevost and Dumas, thirty years since, proved that urea makes its appearance in the blood of animals after the removal of the kidneys; and they concluded that the urea was eliminated by the kidneys, but not produced by them. M. Picard has proved this, by precipitating the urea with nitrate of mercury, by which he can separate the slightest traces of this substance from the blood. The blood of the renal artery of a dog gave 0·0365 per cent. of urea, whilst the renal vein only gave 0·0186 per cent. In man it was found that in the twenty-four hours the arterial blood which passes into the kidneys would give up about 28 grms. of urea; the quantity of urea contained in the urine in the same period varied from 27 to 28 grms.

The urea containing the nitrogenous matter excreted by animals is therefore a direct product of respiration, formed in the blood, like carbonic acid, by slow oxidation by the oxygen of the air furnished by the lungs. From the blood the carbonic acid is eliminated in a gaseous form by the pulmonary surface, and the urea as a soluble product by the kidneys.—*Comptes Rendus*, Sept. 8, 1856, p. 548.

On the Solubility of Oxalate of Lime in Phosphoric Acid.
By C. Neubauer.

I have found that CaO, $\bar{O}$ dissolves in considerable quantity in pure phosphoric acid, especially when heated. If such a solution of freshly precipitated oxalate of lime in phosphoric acid be filtered and diluted with much water (CaO, $\bar{O}$ 0·1 to 0·2 grm. dissolved in PO^5 q. s., HO 500 to 600 cub. centims.), it will remain perfectly clear on cooling, provided there is enough phosphoric acid. If a solution of soda be added gradually in drops to this solution, a point will occur at which the precipitate formed only disappears again slowly; if the mixture be then left standing, it remains clear for some time longer, but turbidity soon appears, and in twenty-four hours the greater part of the dissolved CaO, $\bar{O}$ is crystallized. The supernatant fluid, which is still strongly acid, gives a second, third, &c. crystallization by a further careful addition of solution of soda.

With muriatic acid the experiment did not succeed so well; I did not obtain true, well-developed, quadratic octahedra, the addition of the solution of soda having probably been too rapid.—Liebig's *Annalen*, August 1856, p. 223.

On Caryophyllic Acid. *By* L. Chiozza.

Calvi has repeatedly analysed the caryophyllic acid procured from oil of cloves, in order to test the admissibility of the formula established for it by Gerhardt. The previous analyses made by Dumas, Ettling, and Böckmann gave more carbon than is required according to the formula proposed by Gerhardt. The numbers obtained by Calvi in his analyses differ very little from those required by this formula. The acid employed for analysis was purified by dissolving the crude acid in caustic potash, and boiling the solution until the complete removal of the hydrocarbon which accompanies caryophyllic acid in oil of cloves. The analysis gave—

	Found.					Calculated
	I.	II.	III.	IV.	V.	$C^{20}H^{12}O^4$.
C	72·7	72·4	72·7	72·7	72·6	73·1
H	7·0	7·0	7·0	7·3	7·3	7·3

The equivalent weight of caryophyllic acid cannot be deduced from the density of its vapour, because this acid is altered at a high temperature. Calvi, in several experiments, obtained the same result as Dumas, who gives the density of the vapour of this acid =6·4. The density of vapour calculated from the formula would be 5·66.

The analysis of the baryta-salt gave an amount of baryta which would correspond with the formula $C^{20}H^{12}O^4$; but the analyses of other salts gave variable and contradictory results, as there is great difficulty in preparing these salts in a truly neutral state. Thus the potash-salt always loses a certain quantity of acid during evaporation.

The other experiments made by Calvi confirm the results already obtained by other chemists. The only interesting fact which he ascertained in the investigation of the decomposition of caryophyllic acid is its conversion into a neutral oil by distillation over anhydrous baryta. The product thus obtained is no longer attacked by solution of potash, and has quite different properties from caryophyllic acid, although (if we may conclude from the results of one analysis) it has the same composition and the same density of vapour.—Liebig's *Annalen*, August 1856, p. 242.

On Salicyle Compounds. *By* H. Limpricht.

From Piria's investigation of the compounds of salicylic acid, it appears that this acid is bibasic. The formula of salicylic acid is therefore,—

$$\left.\begin{matrix}C^{14}H^4O^2\\H^2\end{matrix}\right\}O^4,\text{ and not }\left.\begin{matrix}C^{14}H^5O^4\\H\end{matrix}\right\}O^2,$$

and the radical salicyle is $C^{14}H^4O^2$ and not $C^{14}H^5O^4$.

The monobasic acids have only one amide, to be derived from the type NH^3, whilst the bibasic possess three amide compounds, derivable from the types—

$$\begin{matrix}N^2H^2\\H^2\\H^2\end{matrix}\text{, neutral amide; }\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O^2\text{, aminic acid; }\begin{matrix}H\\NH\\H\end{matrix}\text{, imide.}$$

We may therefore conclude from the nature of the amides, whether an acid be monobasic or bibasic.

Hitherto only one amide of salicylic acid, $C^{14}H^7NO^4$, has been known; this was regarded as the neutral amide. Its rational formula was consequently—

$$N\left\{\begin{matrix}C^{14}H^5O^4\\H\\H\end{matrix}\right. .$$

The author now shows that this amide is salicylaminic acid,—

$$\left.\begin{matrix}NH^2(C^{14}H^4O^2)\\H\end{matrix}\right\}O^2,$$

from which the imide, $N\left\{\begin{matrix}C^{14}H^4O^2\\H\end{matrix}\right.$, is easily obtained.

Salicylaminic Acid, $C^{14}H^7NO^4$, is prepared from oil of Gaultheria and concentrated aqueous ammonia. It could not be obtained from salicylate of ammonia, by heating it in a current of ammoniacal gas. The acid crystallizes from boiling water and alcohol in long yellowish laminæ. It fuses at 269°·6 F., and sublimes unaltered in colourless shining laminæ. At 518° F. it boils; water, phenylic alcohol, and carbonate of ammonia are formed. If this treatment be interrupted when one-fourth of the substance is volatilized, the residue consists of salicylimide, $C^{14}H^{5}NO^{2}$, which is formed in the following manner: $C^{14}H^{7}NO^{4}-2HO=C^{14}H^{5}NO^{2}$.

Salicylaminic acid has an acid reaction. Its analysis gave,—

C	61·5	61·5	61·5	14	=	84	61·3
H	5·4	5·6	5·6	7		7	5·1
N	10·3	..	..	1		14	10·3
O	..	..	..	4		32	23·3

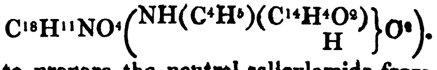
The potash, soda, and magnesia salts were prepared, and the following salts were analysed:—

Strontia-salt.. $C^{14}H^{6}SrNO^{4}$. Copper-salt.. $C^{14}H^{6}CuNO^{4}$.
Lime-salt.... $C^{14}H^{6}CaNO^{4}$. Silver-salt .. $C^{14}H^{6}AgNO^{4}$.

The salts of the alkalies and alkaline earths are crystallizable and very soluble in water. The copper-salt is crystalline; that of silver is grayish-white, amorphous and flocculent.

Salicylimide, $C^{14}H^{5}NO^{2}$.—The residue left when salicylaminic acid is heated to 518° F. is washed with cold alcohol, which extracts any undecomposed salicylaminic acid. A yellowish, microscopic, crystalline powder of salicylimide remains. This is insoluble in water, and scarcely soluble in boiling alcohol and æther. It is dissolved by alcoholic ammonia with a yellow colour, and remains apparently unaltered when this solution is evaporated. With perchloride of iron it acquires a purple colour. Acetate of lead gives a white, sulphate of copper a pale greenish, and solution of silver a yellowish precipitate. Analysis:—

C	70·3	14	=	84	70·6
H	4·4	5		5	4·2
N	11·7	1		14	11·8
O	..	2		16	13·4

Æthylosalicylaminic Acid, 
$C^{18}H^{11}NO^{4}\left(\left.\begin{matrix}NH(C^{4}H^{5})(C^{14}H^{4}O^{2})\\ H\end{matrix}\right\}O^{2}\right)$.
—The author attempted to prepare the neutral salicylamide from the æther. 1st, dry methylosalicylate of potash and iodide of æthyle, and 2ndly, methylosalicylate of baryta and æthylosulphate of potash, were heated on the water-bath in sealed tubes. This process was adopted because, as indicated by Cahours, the neutral æthers of salicylic acid are formed when a salt of methylosalicylic acid is heated with iodide of æthyle or æthylosulphate of potash.

The æther prepared with the first mixture (1) furnished crystals and an oil by treatment with ammonia in twenty-four hours. The crystals were not the neutral amide, but crystals of salicylaminic acid, as the neutral æther employed had an intermixture of methylosalicylic acid. When the oil was heated to 212° F. for some hours with aqueous ammonia, crystals of æthylosalicylaminic acid were obtained.

Crystallized from water, it forms fine colourless needles, which when dried form a light interlaced mass; it is obtained in a more solid form by crystallization from alcohol and æther. It is readily soluble in boiling alcohol and æther, but much less so in the cold. It dissolves readily in boiling water, but scarcely in cold. When boiled with less water than is necessary for its solution, it forms an oil. When heated dry, the acid fuses at 230° F., and solidifies in a crystalline form; it sublimes even at a low temperature. It has a slight acid reaction, and dissolves in hot solution of potash, but separates again on cooling. The aqueous solution is rendered purple by perchloride of iron, and green by sulphate of copper; with acetate of lead it gives a precipitate on the addition of ammonia. The formation of æthylosalicylaminic acid from methylæthylosalicylic æther takes place in accordance with the following equation:—

$$\left.\begin{matrix} C^{14}H^{4}O^{2} \\ (C^{4}H^{5})(C^{2}H^{3}) \end{matrix}\right\} O^{4} + NH^{3} = \left.\begin{matrix} NH(C^{4}H^{5})(C^{14}H^{4}O^{2}) \\ H \end{matrix}\right\} O^{2} + C^{2}H^{4}O^{2}.$$

Analysis:—

C	65·4	65·4	18	=	108	65·4
H	6·6	6·8	11		11	6·6
N	8·5	8·5	1		14	8·5
O	..	..	4		32	19·5

Liebig's *Annalen*, xcviii. p. 256.

ANALYTICAL CHEMISTRY.

On the Volumetric Determination of Ammonia, Carbonic Acid, Alkaline and Earthy Carbonates, Nitrogen, Chlorates, Iodates, Bromates, Nitrates, and Salts of Vegetable Acids by means of Silver. By D. Moha.

The author has extended his mode of volumetric determination of chlorine by means of silver* to the determination of a long series of substances. This is founded upon the fact, that all bodies which may be easily and without loss converted into an equivalent chlorine compound may be most exactly determined by silver, and most readily and exactly by silver and chromate of potash. Berzelius had a great opinion of chloride of silver as the result of a decomposition, and in his determinations of atomic weights preferred employing precipitation with silver. The atomic weight of silver is the most accurately known of all bodies, and chloride of silver has a constant composition, and never carries other bodies down with it.

1. *Ammonia* is slightly supersaturated with muriatic acid, evaporated to dryness without boiling in a sand-bath or drying chamber,

* Liebig's Annalen, xcviii. p. 335.

and mixed with chromate of potash; the chlorine is determined by silver.

2. *Nitrogen.*—When the nitrogen is evolved as ammonia according to the process of Varrentrapp and Will, by calcination with hydrated soda-lime, the ammonia is taken up by muriatic acid, and treated as in No. 1. The weighing of the muriate of ammonia will be much less certain, partly because the weighing in a vessel of the size required for evaporation cannot be effected in small scales, but also because the drying of the muriate of ammonia is more difficult than its deacidification.

3. *Carbonic Acid* is absorbed by chloride of barium and ammonium; the mixture is boiled, filtered, and washed until the fluid running away no longer acts upon silver and red litmus-paper. The carbonate of baryta is dissolved on the filter in dilute muriatic acid, covering it with a watch-glass; the filter is completely washed out, and the fluid passing through is collected in a porcelain dish, and evaporated to dryness. It is dissolved in distilled water, and precipitated with pure carbonate of soda, and at last with some chromate of potash, until the clear fluid appears yellow. The precipitate is thoroughly washed, and the chlorine in the filtrate determined by silver.

4. *Alkaline Carbonates.*—Supersaturation with muriatic acid, drying, and determination of the chlorine.

5. Determination of chloride of sodium and carbonate of soda in mineral waters.

The chlorine in saline waters is determined directly with chromate of potash and solution of silver. The same quantity of the mineral water, after the earths have been precipitated by boiling and filtered, is supersaturated with muriatic acid, evaporated to dryness, and dissolved; the chlorine is determined in the usual way.

6. *Calc-spar, witherite, and strontianite* are converted into neutral chlorides, precipitated by carbonate of soda, washed, and the filtrate determined with chromate of potash and silver.

7. *Carbonate of Ammonia.*

   1. The ammonia as in No. 1.
   2. The carbonic acid as in No. 3.

8. *Free and combined Carbonic Acid in Mineral Waters.*

a. The mineral water is boiled, filtered, and precipitated with chloride of barium. The carbonate of baryta gives the carbonic acid, combined with soda, as chloride of barium, and afterwards as chloride of sodium; or more simply, the boiled mineral water is evaporated to dryness with muriatic acid, and the amount of chlorine is determined after the amount previously present in an equal quantity has been directly determined.

b. An equal volume of mineral water is precipitated with chloride of barium and ammonium; the carbonate of baryta gives the whole quantity of carbonic acid.

The carbonic acid *a*, deducted from *b*, gives the free carbonic acid.

9. *Vegetable Salts of Alkalies and Earths* are destroyed by cal-

cination; the cinder is extracted with muriatic acid, the filtrate evaporated, and the chlorine determined. The exact amount of base is obtained.

10. *Chlorate of Potash*, when free from chloride of potassium, which may be determined alone, is converted into chloride of potassium by calcination or mere heating with pure pyrolusite, and the chlorine determined.

11. *Hyperchlorate of Potash* is treated in the same way. A reaction with sulphuric acid shows which salt is present.

12. *Neutral Nitrates* are converted into chlorides by boiling with an excess of muriatic acid. Existing chlorides may be previously determined by themselves.

No acids which may be expelled by muriatic acid should be present,. This determination must always be made with great care. A great number of cases may also be introduced into this analysis.

The question whether this method gives correct results coincides with that, whether a compound may be converted into an equivalent quantity of a chloride, as the employment of the method depends upon the determination of chlorine. When carbonate of soda is evaporated to dryness with muriatic acid, an equivalent quantity of chloride of sodium must be produced, and the determination of the chlorine is as certain a determination of the soda, as the alkalimetric one with acids.

0·5 grm. of chemically pure, freshly heated carbonate of soda was exactly weighed, and converted into chloride of sodium; the evaporation took place in a hot chamber, and the dissolved saline mass was quite neutral. The fluid was put into a glass of 300 cub. centims., filled up to the mark, and shaken round. 100 cub. centims. of this fluid were taken out with a pipette, and the amount of chlorine determined with silver and chromate of potash. For 100 cub. centims.—

1. 31·5 cub. centims. of normal silver solution $\left(\frac{1}{10000}\right)$,
2. 31·5 cub. centims. of normal silver solution $\left(\frac{1}{10000}\right)$,

were employed; for the whole quantity, therefore, 94·5 cub. centims. This number, multiplied by the ten-thousandth of the atomic weight, gives the corresponding compound in grammes. For carbonate of soda (1 atom=53), this is 0·0053, and 0·0053 × 94·5 gives 0·50085 grm. of carbonate of soda.

This analysis however contains at once a determination of carbonic acid, soda, chlorine and chloride of sodium; carbonic acid and soda as constituents of the substance examined, chlorine as combined with the sodium of the carbonate, and chloride of sodium as produced. Therefore by multiplying 94·5 by 0·0022 (carbonic acid), 0·0031 (soda), 0·003546 (chlorine), and 0·005846 (chloride of sodium), we get the following results:—

	Calculated from formula	Found.
Carbonic acid........	0·2075	0·2079
Soda	0·29245	0·29295
Chlorine	0·3345	0·3350
Chloride of sodium....	0·5515	0·5524

And considering the carbonic acid as produced by the combustion of carbon, we get, by multiplying with 0·0006,—

	According to formula.	Found.
Carbon ……	0·0566	0·0567

This shows the possibility of determining the carbon obtained in analyses by combustion in this manner.

1 grm. of dry carbonate of baryta was dissolved in muriatic acid, evaporated to dryness, sharply heated, then dissolved, decomposed by chromate of potash, and filtered into a bottle of 300 cub. centims. 100 cub. centims. of this fluid required 34 cub. centims. of normal silver solution, or 102 cub. centims. for the whole; this gives—

	Employed.	Found.
Carbonate of baryta ………	1 grm.	1·005618 grm.
Carbonic acid …………	0·2231 grm.	0·2244 grm.

Liebig's *Annalen*, xcix. August 1856, p. 197.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

New Process for the Preparation of Ferrocyanide of Potassium.

By RICHARD BRUNNQUELL.

THIS process depends on the conversion of ammonia into cyanide of ammonium by ignition with charcoal or carbonaceous matters; and its principal peculiarity consists in the conversion of the cyanide of ammonium thus produced into cyanide of potassium, representing ferrocyanide of potassium, in the humid way. The gas containing ammonia is therefore passed through tubes filled with charcoal and heated to redness; the ammonia is thus converted into cyanide of ammonium, and this into ferrocyanide of potassium by contact with aqueous solutions of potashes and suitable iron compounds. The particular advantages of this method are the following:—

1. *The considerable loss of potash and the expense of its recovery are got rid of.*—The potashes are first dissolved in water, by which they are freed from the greater part of the foreign salts. The solution is then treated with a quantity of the cyanide sufficient to convert the greater part of it into ferrocyanide of potassium; this is allowed to crystallize, and the mother-liquor employed without further preparation for the same purpose. Thus we get rid at once of the contamination with silica, &c., and of the necessity of bringing the dissolved potashes again into a solid form, which is of itself a cause of loss.

2. *It becomes possible to replace the potashes by soda, which is much cheaper.*—By the old processes this was often tried in vain, because from the difficult reduction of sodium the formation of cyanide of sodium in the dry way does not take place so easily, and moreover ferrocyanide of sodium cannot easily be crystallized from such impure solutions as the mother-liquors. The first difficulty is entirely got rid of in its formation in the humid way, and the second may also be overcome, as the solutions are much purer. Ferro-

cyanide of sodium certainly does not form such beautiful crystals as ferrocyanide of potassium; but if it can be prepared more cheaply, it will certainly make its way into use, especially as 6 parts of it go as far as 7 of ferrocyanide of potassium, the equivalent of sodium being lower.

3. *Bones may be employed in this process*, their subsidiary product, bone-charcoal, covering the cost of the bones and their carbonization, and they would therefore furnish the nitrogenous gases for nothing. The gases from the carbonization of bones are just as rich in ammonia in proportion as those of most other raw materials; in proportion to their weight however bones furnish less ammonia and much less gas.

4. *It is possible to bring back into the manufacture that portion of the ammonia which escapes conversion into cyanogen*, and thus convert it also into cyanogen; the ammoniacal salts obtained as subsidiary products may be converted into ferrocyanide of potassium by mixing them with lime, and adding them to the raw material. In this process the following questions arise:—

1. *Does this conversion take place without difficulty in such proportion that the cyanides may be obtained thereby?*—According to Langlois, cyanide of ammonium is produced in considerable quantity, and with evolution of H^2C and H, by the contact of ammonia with incandescent charcoal. It is also produced when carbonate of ammonia, or any nitrogenous organic compound, is passed with a hydrocarbon, or, if the compound contain hydrogen, with carbonic oxide gas through a red-hot tube. Kuhlmann confirms these statements, and has already made use of the cyanide of ammonium thus obtained in the preparation of anhydrous hydrocyanic acid, by passing it through heated and somewhat dilute sulphuric acid. Gmelin says that cyanide of ammonium is prepared by passing ammonia over red-hot charcoal, and also by the ignition of ammonia with organic compounds, with hydrocarbons, carbonic oxide gas, and even with graphite. That this formation does not take place with difficulty is also proved by the production of cyanide of ammonium from carbonic oxide gas and ammonia, or the gaseous oxides of nitrogen and vapour of alcohol by the action of spongy platinum.

2. *Are the other gases mixed with the ammonia in the gases injurious to this process?*—That this question is to be answered in the negative appears from what has been stated in the last paragraph. If carbonic oxide gas, hydrocarbons, and carbonic acid are capable of inducing this process and entirely replacing the charcoal, it is impossible that they can prevent it in any way. The best proof is that common coal gas contains cyanide of ammonium. If we consider that in the manufacture of gas a great portion of the ammonia escapes before the coal is sufficiently heated, that a great portion of the gas (which is evolved in the neighbourhood of the conducting tube) has only to pass a short distance through the red-hot coals, and lastly, that the amount of nitrogen in coals is very small and the excess of foreign gases very considerable, it must be a

matter of surprise that so much cyanide of ammonium can be formed. Carbonic acid perhaps may play a peculiar part in this case. The gases certainly contain no free carbonic acid, but only carbonate of ammonia, which is converted into cyanide of ammonium, $2NH^4O + CO^2 = NH^4C^2N, 4HO\,(2O)$. But when they had passed through the red-hot tube, they always contained much carbonic acid, and the solution of potash through which they passed was always converted into carbonate. The author thinks that this can only be derived from the decomposition of aqueous vapour, which, as is well known, furnishes carbonic acid as well as hydrogen and carbonic oxide gases by contact with red-hot charcoal. The carbonic acid produced in this, or any other manner, would certainly decompose cyanide of ammonium (just like cyanide of potassium), producing hydrocyanic acid and carbonate of ammonia, which would again furnish cyanide of ammonium, &c. This however is just what is desired. If cyanide of ammonium be obtained as a product of this process, exactly half the nitrogen is lost for the formation of ammonium, which is not the case if carbonic acid has the action above described; its action therefore can only be regarded as favourable.

As the author passed to his direct experiments upon this formation, especially with regard to quantity, he observed that these did not always give exactly the desired result, which at all events partly depends on the method employed. Thus not being yet acquainted with the peculiar action of carbonic acid, he passed the gases containing cyanide of ammonium into solution of potash containing suspended hydrate of protoxide of iron. As however potash always contains a great deal of carbonic acid, it is possible that a portion of the hydrocyanic acid would be again expelled by it. The experiments varied considerably in their results; as the average of the most certain ones the author gives 10 to 12 per cent. of ferrocyanide of potassium from blood; particular experiments gave a much higher result. Although the author has no doubt that by operating on a larger scale, and with more complete arrangements and better observations as to the most advantageous treatment (the proper temperature, duration, &c.), a very different result would be obtained, and although a new process never comes out quite perfect, he makes a deduction from it, and seeks to prove that even with an equal result (or an average of 10 per cent.) the totally independent advantages above described would alone secure the new process a better œconomical result. He does not however give up the hope of succeeding in converting nearly the whole of the nitrogen into cyanide of ammonium.

3. *Does the conversion of the cyanide of ammonium into ferrocyanide of potassium take place without loss, and how is it best effected?*—The simplest plan, of course, would be (as previously recommended by Binks) to effect the conversion by means of an aqueous solution of potashes. This however is impossible, as carbonate of potash is not decomposed either by hydrocyanic acid or by cyanide of ammonium; caustic potash also cannot be employed, on account of the excess of carbonic acid in the gases. This con-

version therefore requires the intervention of another body, and for this purpose the author selects sulphate of iron. If cyanide of ammonium or hydrocyanic acid and carbonate of ammonia be passed into an excess of solution of sulphate of iron, sulphate of ammonia and protocyanide of iron are always produced. Thus, in the first place, all the ammonia is obtained as sulphate, by which the sulphate of iron is abundantly paid for; and in the second the cyanide of ammonium is instantaneously converted into an insoluble and undecomposable compound, from which ferrocyanide of potassium or sodium may be obtained by treatment with alkaline carbonates.

As regards the carrying out of the process on a large scale, the carbonization of course differs from that now used, inasmuch as in the present case as much as possible of the nitrogen must be driven off in the gaseous form, whilst in the other the object is to obtain a coal as rich as possible in nitrogen. If bones be employed, the quality of the bone-charcoal to be produced must alone give the rule; and it is, in fact, of no consequence if a small per-centage of nitrogen does remain in it, as the bone-charcoal will at least pay for it, even when in the production of great quantities no direct gain is thereby attained. The goodness of bone-charcoal depends,—1st, on the fat being left in the bones; 2ndly, on the carbonization being complete; and 3rdly, on the avoidance of a high pressure of gas during the process. In employing other raw materials, lime must be used to assist in the expulsion of the nitrogen; the substance must first be carbonized alone, so that a readily triturable coal is obtained, and this is then intimately mixed with powdered hydrate of lime, and again distilled. The residue will furnish an excellent manure.

The carbonizing furnace should be arranged exactly like a gas-furnace, the number and size of the retorts depending on the amount of the charge. The conducting tubes of all the retorts open first, as in the gas-furnaces, into a common horizontal cylinder, into which they are fixed with tar. Here the products are mixed, and conducted hence to the earthen tubes, by which the advantage is gained that the passage of the gases through the latter is uniform. When each retort is united with a fire-clay tube, the passage of the gases takes place far too rapidly at the commencement of the process, and too slowly towards its end. If, on the contrary, three retorts are combined, and six hours are required to work them off, one is set to work every two hours, and not all at once. The tubes leading from the mixing cylinder are each furnished with a cock, to enable each tube to be closed at pleasure in case of any damage; these tubes also should be at least 2 inches in internal diameter, as short as possible, and accessible on all sides.

The conversion of the ammonia into cyanide of ammonium takes place as the gases pass through red-hot earthen tubes, filled with fragments of charcoal of the size of a nut. Numerous experiments showed that iron tubes are not applicable to this purpose, as cyanide of ammonium and hydrocyanic acid, like gaseous cyanogen, are decomposed into their elements by contact with red-hot iron, with formation of carburet of iron. Three experiments with gun-barrels furnished no trace of cyanide of ammonium. On the large scale, the author has been constantly endeavouring to bring iron tubes into use by lining them with an indifferent substance, especially with charcoal, by repeatedly coating them with tar, and burning coals in them. The result was however insufficient (about 4 per cent.), probably however merely because, not being at the time aware of the presence of a large quantity of carbonic acid, the author employed solution of caustic potash for the absorption of the cyanide of ammonium, by which means not only monocarbonate, but even bicarbonate of potash was formed. The best plan was the incrustation of the iron tubes by the repeated application of a mixture of ox-blood and clay, and gradually heating each layer as applied. In the first experiment with tubes thus prepared, they were burnt through, so that although it may not be impossible to bring iron tubes into use, yet the clay tubes deserve the preference. These only differ from the common gas-retorts in their smaller diameter, and in the adaptation of their two ends for the reception of iron heads. The narrower and longer they can be prepared the better; those employed by the author were 4 inches in internal diameter and 6 feet long. The arrangement of the furnace in this case would also be exactly the same as that of a gas-furnace, the requirements in both cases being the same, namely, the application of a uniform heat to the whole length of a number of these tubes with the smallest quantity of fuel. For the present purpose the author considers that one of the best furnaces is the English gas-furnace for the combined employment of iron and earthen retorts, as described by Croll.

With this arrangement, seven retorts and six earthen tubes would be heated by the same fire. The charging of the tubes with charcoal is indeed not absolutely necessary, as the foreign gases mixed with the ammonia are capable of furnishing the carbon necessary for the formation of cyanogen, which however is assisted by the action of the charcoal as a porous mass. The waste of charcoal is for this reason extremely small; it is sufficient from time to time to press the charcoal together and add a little fresh. Perforated clay discs are placed at the two ends of the tubes, to prevent the obstruction of the conducting tubes in the iron heads. Before the passage of the gases commences, care must be taken that the tubes are quite red-hot, as otherwise, besides the actual loss, tarry vapours pass through without decomposition, and contaminate the fluids which pass subsequently. A very bright red heat is the temperature necessary for the formation of cyanogen. As in the previous methods the fusion is the principal point, so here everything depends upon the correct conduct of this operation.

The conversion of cyanide of ammonium into cyanide of potassium or ferrocyanide of potassium is effected by the mediation of sulphate of iron. In practice, the difficulty here consists in producing a complete absorption of the cyanide of ammonium, by means of the long contact of the gases with the solution of sulphate of iron, without thereby causing a great pressure of gas, as experiments have shown that the quality of the bone-charcoal is injured by this means, and the loss by escape increases with the pressure. The author has employed an apparatus, which from its simplicity and the ease with which its efficiency may be increased, appears admirably adapted for this and similar purposes. This consists of a chest 6 feet long, 2 feet broad, and 8 inches deep, in the interior of which there are four shallow trays of the same size, but only 2 inches deep, placed one above the other, with their hollow surfaces turned downwards. Each of these trays exhibits an opening at one end, forming a communication between its interior and that of the one above it, and these apertures are placed alternately at one end or other of the trays. The chest is then filled with fluid, and gas is allowed to enter beneath the lowest of the partitions, where it forms a constantly increasing bubble (like the air-bubbles under ice) until it reaches the openings at the end of the tray, through which it then rises in separate bubbles, to go through the same course under the second, third, and fourth trays. Theoretically, there is thus constantly a stratum of gas of $4 \times 8 = 48$ feet in contact with the fluid, and the distance passed through by the gas is 24 feet, but the pressure is not more than that of a column of fluid of not quite 8 inches in height. The apparatus also requires,—1st, a cock to let the fluid run off; 2ndly, a funnel for filling it, reaching a little below the surface of the fluid; 3rdly, an escape-tube for the gas, which conducts it to the furnace for combustion, and in which, to avoid explosions, a box filled with fine wire-net is placed. In particular cases like the present, in which a precipitate is formed, it is advisable to have a little stirring apparatus in each compartment, passing through tight boxes in the partitions. It is better, in place of one large apparatus, to use two smaller ones, passing the fluid from the second to the first, by which it becomes possible to precipitate the whole of the solution of sulphate of iron without losing any cyanide of ammonium. The fluid drawn off from the first chest thus consists essentially of sulphate of ammonia and suspended protocyanide of iron + hydrated protoxide of iron and a little sulphuret of iron. These are separated by deposition and filtration; the somewhat concentrated solution of sulphate of ammonia is evaporated, and the salt is either sold to the alum-works, or mixed with lime and added to the animal substances, to be again converted into cyanogen. The washing-water serves for the solution of fresh quantities of sulphate of iron. The washed precipitate is boiled with solution of potashes, and thus converted into ferrocyanide of potassium, and the residue is either thrown away or dissolved in muriatic acid, when this is to be had, to serve instead of sulphate of iron.

The crystallization and preparation of the ferrocyanide of potassium in the commercial form now presents no difficulty, as we have to do with far purer materials. When the iron deposit is properly washed and boiled with a solution of purified potashes, a solution is obtained, which, in addition to ferrocyanide of potassium, only contains a little excess of carbonate of potash, from which the commercial salt may be prepared by a single crystallization. The author therefore has no doubt that the employment of soda is thus rendered possible; and experiments on a pretty large scale gave a citron-yellow salt, although in rather small crystals. The iron deposit remaining undissolved after boiling with the alkaline solution must of course be filtered and washed. The washing-waters serve for the dilution of the solution of potashes, and the mother-liquors are employed without further treatment for the same purpose.

In conclusion, if we compare the old and new processes together in a more practical point of view, we find,—

1. That there is a saving of labour. The process of fusion, which always requires two workmen, is got rid of; a single workman can attend to two furnaces with a great number of earthen tubes, as he has only to keep up the supply of fuel, and open the tubes every two or three days to put in some fresh charcoal. The labour connected with the treatment with sulphate of iron is abundantly outweighed by the lixiviation, filtering, and washing of the carbonaceous residue, and the whole of the work required for the recovery of the salt in the mother-liquors is got rid of.

2. The expenditure of fuel will certainly be greater, as the formation of cyanogen takes place more slowly in this way; but even if it be supposed double, this disadvantage will be far more than compensated for by the advantages.

It is not to be denied that the process has its difficulties; but when these are overcome, the considerable saving in potashes, and the possibility of replacing this by soda, will at once bring the calculation in favour of the new process.

The author mentions, in conclusion, that by the method proposed by him, that is to say the separation of the production of cyanogen, from its combination with the fixed alkalies, it may perhaps be possible to make use of the nitrogen of the air. In experiments on the production of cyanogen from the atmospheric nitrogen, it was observed by Wöhler, Erdmann, and Marchand, that this only succeeded in the presence of aqueous vapour. This and similar observations induced many chemists to suppose that in this case a preliminary formation of ammonia must always take place. Direct experiments have now confirmed the production of ammonia from free nitrogen and aqueous vapour by means of red-hot charcoal. Fleck has also communicated to the author some experiments in which he obtained tolerable quantities of ammonia in this way, although in some cases its formation did not take place from some unknown cause. But would it not be more rational to study this mode of formation exactly, and then to produce it directly by mixing the nitrogen with the proper quantity of aqueous vapour, and converting the ammonia thus obtained into cyanide of ammonium? We should thus get over the greatest practical difficulty in the preparation of cyanide of potassium from the atmospheric nitrogen, namely, the destruction of the earthen tubes or walled pits by the fusing potashes.—*Polyt. Centralblatt,* 1856, p. 670 and 744.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 19, 1856. (The Lord Wrottesley, President, in the Chair.)

"On some Compounds of Ethylene." By H. L. Buff.

Among the hydrocarbons which are capable of replacing hydrogen, the radicals of the general formula $C_n H_{(n+1)}$, *i. e.* the homologues of ethyle, are best examined. There is another class of hydrocarbons which may be represented by the general formula $C_n H_{(n-1)}$. The only well-known term of this series is the radical allyle, $C_6 H_5$, to which the attention of chemists has been especially called of late by the researches of Messrs. Hofmann and Cahours on allylic alcohol. These researches have established the most perfect parallelism between the two classes of radicals and their derivatives. Both the radicals $C_n H_{(n+1)}$ and $C_n H_{(n-1)}$ are *monatomic*, i. e. molecules capable of replacing 1 equiv. of hydrogen.

These two classes stand in the closest relation to each other, and it is by no means improbable that one class may pass over into the other, for instance, that the radical propyle $C_6 H_7$, or a propyle-compound, may be converted into allyle or an allyle-compound.

There exist a third series of hydrocarbons, which, again, both by composition and origin, are closely allied to the former two. They are represented by the general formula $C_n H_n$; and methylene, $C_2 H_2$, ethylene, $C_4 H_4$, and propylene, $C_6 H_6$, are well-known terms belonging to this series. These hydrocarbons are also radicals; they differ, however, in their nature essentially from those of the former groups, inasmuch as they are *biatomic* molecules, *i. e.* molecules capable of replacing 2 equivs. of hydrogen.

There exist parallel with these three series of radicals which form *alcohols*, three other groups of radicals, which *in acids* play exactly the same part that in the *alcohols* is assigned to the hydrocarbons. These acid-forming radicals contain, in addition to carbon and hydrogen, oxygen and other elements belonging to the oxygen group. They are closely connected with the radicals of the alcohols, and this close connexion is particularly well established between the first series of alcohol-forming radicals and the corresponding series of acid-forming radicals.

Methyle, $C_2 H_3 - 2H + 2O =$ Formyle, $C_2 HO_2$

Ethyle, $C_4 H_5 - 2H + 2O =$ Acetyle, $C_4 H_3 O_2$

Propyle, $C_6 H_7 - 2H + 2O =$ Propionyle, $C_6 H_5 O_2$.

Formic, acetic and propionic acids are formed by the imperfect oxidation of methyle-, ethyle- and propyle-alcohol, and we may consider them to be simple substitution-products of these alcohols.

By means of the electric current we are able to produce ethyle, methyle and hydrogen from propionic, acetic and formic acids, and these acids we may reproduce again by the action of hydrate of potassa on the cyanogen compounds of hydrogen, methyle and ethyle.

Both series of radicals are chained together by these reactions, and we may view acetyle and propionyle as formyle, the hydrogen of which is replaced by methyle and ethyle.

Formyle .... $=C_2(H)O_2$
Acetyle .... $=C_2(C_2H_3)O_2$
Propionyle ...... $=C_2(C_4H_5)O_2$.

There is no doubt that the same relation exists between the hydrocarbons of the other series of radicals and the radicals of the corresponding acids, between allyle, C_6H_5, and the radical of acrylic acid, acryle $C_6H_5O_2$, and between methylene, C_2H_2, ethylene, C_4H_4, propylene, &c., and the radicals of the bibasic acids, which are homologues of succinic acid, $C_8H_6O_8$.

The biatomic radicals are in general far less studied than the monatomic radicals; still they occur in many compounds, and are met with in different departments of chemistry.

In addition to the terms already mentioned, we find them in the phenyle, benzyle, naphthyle and other series.

In the hope of adding some facts to the history of the polyatomic radicals, I have made some experiments with chloride of ethylene, $C_4H_4Cl_2$.

This compound, as well as the bromide of ethylene, refused to act in many instances; in others it underwent the same change which is induced by the action on it of a solution of potassa in alcohol, splitting into the compound C_4H_3Cl and hydrochloric acid.

On boiling chloride or bromide of ethylene with an alcoholic solution of sulphocyanide of potassium, a very definite reaction takes place. The change being completed, the alcohol is separated by distillation, and the residue treated with a small quantity of cold water in order to remove chloride or bromide of potassium, which is produced, and the excess of sulphocyanide of potassium. The more or less coloured residue is then dissolved in boiling alcohol, and the solution, after digestion for some time with animal charcoal and a few drops of hydrochloric acid, filtered whilst hot. This solution deposits on cooling fine white, very brilliant and large rhombic plates of a hard and brittle substance*.

The analysis of this substance leads to the formula $C_4H_4Cy_2S_4$, and its formation may be represented by the equation

$$C_4H_4Cl_2+2KCyS_2=2KCl+C_4H_4Cy_2S_4.$$

Sulphocyanide of ethylene fuses at 90° C. and solidifies at 83°. It is but slightly soluble in cold water, more so in boiling water, from which it crystallizes in groups of needles. It is decomposed at a higher temperature, and evolves a highly pungent vapour, the odour of which very much resembles that of burnt onions. On boiling a solution of sulphocyanide of ethylene in water, a very acrid odour is observed, which produces lacrymation and violent sneezing. Sulphocyanide of ethylene has a sharp taste, causing a burning sensation in the throat.

Solution of ammonia decomposes sulphocyanide of ethylene even at the common temperature. A flocculent substance separates, and the solution contains several compounds which I have been unable to separate.

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* Whilst M. Buff was engaged with these researches, M. Sonnenschein has communicated some experiments made in the same direction, which have likewise led to the discovery of this substance. Sonnenschein's results, which are published in the Journ. für Prakt. Chem. June 1855, came to our knowledge only after a summary of the results had been sent to the editor of the Annalen der Chem. und Pharm.—A. W. H.

At the temperature of boiling water sulphocyanide of ethylene mixes with aniline in every proportion; no reaction, however, is perceptible. But on boiling the mixture decomposition sets in, and a volatile substance is evolved which restores the colour of reddened litmus paper.

When boiled with solution of hydrate of baryta and oxide of lead or mercury, sulphocyanide of ethylene loses its sulphur; the substance left behind possesses very little power of crystallizing. In the case of oxide of mercury, besides sulphide of mercury and carbonate of barium, a difficultly soluble body containing mercury is formed.

At the temperature of boiling water, sulphocyanide of ethylene dissolves readily in very dilute nitric acid; on cooling of the solution the substance is deposited unchanged. On treating it with stronger nitric acid a decomposition takes place, and a crystalline acid is formed. This acid is best produced by heating sulphocyanide of ethylene on the water-bath with dilute nitric acid as long as red fumes of nitrous acid are evolved. The residue is a strongly acid syrup, which becomes finally crystalline. It is repeatedly dissolved in water and evaporated on the water-bath in order to expel the nitric acid. Thus purified, the new acid is dissolved in boiling water, neutralized with pure carbonate of barium and separated from sulphate of barium. On cooling, the barium-salt of the new acid crystallizes. It is soluble in boiling water, less so in cold water, and almost insoluble in alcohol, by means of which it may be precipitated from its solution in water.

On examining the appearance and deportment of this salt, Dr. Hofmann, in whose laboratory I performed these experiments, at once recognized the identity of this compound with the barium-salt of disulphetholic acid which he and Mr. Buckton have lately discovered.

This view was fully confirmed by the analysis which I made.

The composition of the barium-salt, dried at 160°, is represented by the formula

$$C_4\,(H_4\,Ba_2)\,S_4\,O_{12}.$$

The potassium salt of this acid is readily soluble in water; it crystallizes easily, and is likewise precipitated by alcohol from its solution in water. Dried at 100° C., it contains

$$C_4\,(H_4\,K_2)\,S_4\,O_{12}.$$

At 160° it suffers no decomposition; when exposed to a higher temperature, however, it blackens and intumesces, empyreumatic substances being evolved.

It is obvious that this bibasic acid stands in the same relation to ethylene as the monobasic ethylsulphurous acid to ethyle.

The origin of the two acids is perfectly analogous, the latter acid, according to Mr. Muspratt, being obtainable also by the action of nitric acid upon sulphocyanide of ethyle.

Sulphocyanide of ethyle, $C_4\,H_5\,Cy\,S_2$, produces ethylosulphurous acid, $C_4\,H_5, H, S_2\,O_6$.

Sulphocyanide of ethylene, $C_4H_4Cy_2S_4$, produces ethylensulphurous acid, C_4H_4, 2H, $2S_2O_6$.

This reaction appears to throw some light upon the constitution of polybasic compounds. The compounds of monatomic molecules of the hydrogen-group with elements or compound radicals of the oxygen-group, are all remarkable for the simplicity of their construction. The union of biatomic radicals of the hydrogen-group with molecules of the oxygen-group gives rise to combinations of a far more complicated character. Whilst one molecule of water, H_2O_2, most conveniently may be considered as the type of many compounds of the former class, the corresponding compounds of biatomic radicals frequently correspond to a double molecule of water, $2H_2O_2$.

Sulphocyanide of potassium may be viewed as water, in which the oxygen is replaced by sulphur, one of the hydrogen molecules by cyanogen, the other by potassium.

$$\text{Water}\ \left.\begin{array}{c}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O_2}\qquad\text{Sulphocyanide of potassium}\ \left.\begin{array}{c}\mathrm{Cy}\\ \mathrm{K}\end{array}\right\}\mathrm{S_2}$$

In the production of sulphocyanide of ethylene two equivalents of chlorine in chloride of ethylene ($C_4H_4Cl_2$) have to be eliminated by two equivalents of potassium. Thus the very reaction of the two factors, chloride of ethylene ($C_4H_4Cl_2$), and two equivalents of sulphocyanide of potassium $2(KCyS_2)$, joins 4 equivs. of sulphur and 2 equivs. of cyanogen with one molecule of ethylene. This reaction may be expressed by the following equation, which will illustrate at once my view in regard of the constitution of this substance;—

$$\begin{array}{l}\left.\begin{array}{c}\mathrm{Cy}\\ \mathrm{K}\end{array}\right\}\mathrm{S_2}\\ \left.\begin{array}{c}\mathrm{K}\\ \mathrm{Cy}\end{array}\right\}\mathrm{S_2}\end{array} + \mathrm{C_4H_4Cl_2} = \begin{array}{c}\mathrm{Cy}\\ \mathrm{C_4H_4}\\ \mathrm{Cy}\end{array}\begin{array}{l}\left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2}\\ \left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2}\end{array} + 2\mathrm{KCl}.$$

The acid produced by the action of nitric acid upon sulphocyanide of ethylene obviously belongs to the same type. In this compound, which in the conception of this view may be called *ethylene-sulphurous* acid, the cyanogen is replaced by hydrogen, whilst the sulphur has been oxidized into the compound radical S_2O_6, which in sulphurous acid we assume united with hydrogen.

$$\begin{array}{c}\text{Two}\\ \text{mole-}\\ \text{cules of}\\ \text{water.}\end{array}\begin{array}{l}\left.\begin{array}{c}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O_2}\\ \left.\begin{array}{c}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O_2}\end{array}\qquad\begin{array}{c}\text{Two equivs.}\\ \text{of bisulphite}\\ \text{of potas-}\\ \text{sium.}\end{array}\begin{array}{l}\left.\begin{array}{c}\mathrm{H}\\ \mathrm{K}\end{array}\right\}\mathrm{S_2O_6}\\ \left.\begin{array}{c}\mathrm{H}\\ \mathrm{K}\end{array}\right\}\mathrm{S_2O_6}\end{array}\qquad\begin{array}{c}\text{Ethylene-}\\ \text{sulphu-}\\ \text{rous}\\ \text{acid.}\end{array}\begin{array}{c}\mathrm{H}\\ \mathrm{C_4H_4}\\ \mathrm{H}\end{array}\begin{array}{l}\left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2O_6}.\\ \left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2O_6}.\end{array}$$

Since we find that the hydrogen-molecules in polybasic acids are replaceable by two or more molecules of different metals or radicals,—witness tartrate of potassium and sodium, oxalovinate of potassium,—the idea naturally suggests itself that the biatomic alcohol-forming radicals may be capable of uniting two molecules of different elements or compounds of the oxygen-group. It is probable, for instance, that the ethionic acid, discovered by M. Magnus, may be such a compound, namely *ethylene-sulphuro-sulphurous acid.*

$$\begin{array}{c}\text{Disulphetholic}\\ \text{acid.}\end{array}\ \begin{array}{c}\mathrm{H}\\ \mathrm{C_4H_4}\\ \mathrm{H}\end{array}\begin{array}{l}\left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2O_6}\\ \left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2O_6}\end{array}\qquad\begin{array}{c}\text{Ethionic}\\ \text{acid.}\end{array}\ \begin{array}{c}\mathrm{H}\\ \mathrm{C_4H_4}\\ \mathrm{H}\end{array}\begin{array}{l}\left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2O_6}\\ \left.\vphantom{\begin{array}{c}X\\X\end{array}}\right\}\mathrm{S_2O_8}\end{array}$$

The following Table contains some of the known ethylene and succinyle compounds compared with the corresponding derivatives of the ethyle and propionyle series.

Compounds of the Alcohol-forming Radicals.

Ethyle-series.		*Ethylene-series.*	
Ethyle	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}$	Ethylene	C_4H_4
Chloride of ethyle	C_4H_5Cl	Chloride of ethylene..	$C_4H_4Cl_2$
Sulphide of ethyle	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}S_2$	Sulphide of ethylene..	$C_4H_4S_2$
Mercaptan	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2$	Ethylene-mercaptan..	$\begin{array}{l}H\\C_4H_4\\H\end{array}\begin{array}{l}\}S_2\\\}S_2\end{array}$
Sulphocyanide of ethyle.	$\left.\begin{matrix}C_4H_5\\Cy\end{matrix}\right\}S_2$	Sulphocyanide of ethylene.	$\begin{array}{l}Cy\\C_4H_4\\Cy\end{array}\begin{array}{l}\}S_2\\\}S_2\end{array}$
Bisulphide of ethyle.	$C_4H_5S_2$	Bisulphide of ethylene	$C_4H_4S_4$
Ethylsulphurous acid.	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2O_6$	Ethylene-sulphurous acid.	$\begin{array}{l}H\\C_4H_4\\H\end{array}\begin{array}{l}\}S_2O_6\\\}S_2O_6\end{array}$
————————		Ethylene-sulphuro-sulphurous acid.	$\begin{array}{l}H\\C_4H_4\\H\end{array}\begin{array}{l}\}S_2O_6\\\}S_2O_8\end{array}$
Sulphovinic acid	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2O_8$		

Compounds of the Acid-forming Radicals.

Propionyle-series.		*Succinyle-series.*	
Chloride of propionyle.	$C_2(C_4H_5)O_2,Cl$	Chloride of succinyle.	$C_4(C_4H_4)O_4,Cl_2$
Propionyle-series.		*Succinyle-series.*	
Propionic acid..	$C_2(C_4H_5)\left.\begin{matrix}O_2\\H\end{matrix}\right\}O_2$	Succinic acid..	$\begin{array}{r}H\\C_4(C_4H_4)O_4\\H\end{array}\begin{array}{l}\}O_2\\\}O_2\end{array}$
Anhydrous propionic acid.	$\left.\begin{matrix}C_2(C_4H_5)O_2\\C_2(C_4H_5)O_2\end{matrix}\right\}O_2$	Anhydrous succinic acid.	$C_4(C_4H_4)O_4,O_2$
Propionylamide	$N\left\{\begin{matrix}H\\H\\C_2(C_4H_5)O_2\end{matrix}\right.$	Succinamide.	$\left.\begin{matrix}N\left\{\begin{matrix}H\\H\end{matrix}\right.\\ C_4(C_4H_4)O_4\\ N\left\{\begin{matrix}H\\H\end{matrix}\right.\end{matrix}\right.$

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Tantalum and its Compounds. By H. Rose.

For the preparation of metallic tantalum, the compound of fluoride of tantalum and fluoride of sodium was employed, of which 3 parts were put in layers with 1 part of sodium into a closely covered iron crucible, and heated. At a dull red heat, as the action of the sodium upon the salt took place, the mixture became strongly incandescent. The heat was then continued for a short time, and the crucible was quickly cooled. It contained a black mass, from which, when put into water, a black powder separated, which must be washed with water as long as the latter removes any salt, and finally completely washed with dilute alcohol.

The black powder is metallic tantalum, but usually not perfectly pure. It contains acid tantalate of soda, with which it is less contaminated when a protective covering of chloride of potassium is employed in its preparation.

Berzelius employed essentially the same method in the preparation of tantalum. According to him, however, it is not a conductor of electricity, whilst the metal prepared by the author, although it was not quite pure, conducted electricity very well. When heated in the air, it burns with a brilliant lustre, but is oxidized with some difficulty, and only by frequent stirring with a platinum wire during incandescence, forming white tantalic acid. It is not attacked by muriatic acid, nitric acid or nitromuriatic acid, even by long contact and boiling, as was already observed by Berzelius. When heated with hydrofluoric acid, it is slowly dissolved, partly with evolution of gas; but even after long heating a grayish residue remains obstinately insoluble. But if hydrofluoric acid be poured over tantalum, and nitric acid be then added, solution takes place rapidly on the application of heat, with evolution of red fumes. Tantalum is not dissolved by sulphuric acid, even when concentrated, with the assistance of heat. By long fusion with bisulphate of potash, however, it is oxidized to tantalic acid.

Berzelius found that the tantalum prepared by him, when converted into tantalic acid by calcination in the air, obtained an increase of weight of 17·0, 15·84, and 15·33 per cent. Hence tantalic acid would contain 14·53, 13·69, and 13·29 per cent. of oxygen, whilst he himself only admits in it 11·51 per cent. He attributes the greater increase of weight to the presence of silica in his tantalum. Of the tantalum prepared by the author, 100 parts when calcined only took up 12·81 parts of oxygen. This corresponds with an amount of 11·36 per cent. of oxygen in the tantalic acid, which certainly agrees better with the supposition of Berzelius than his own experiments, but still presupposes a somewhat less pure tantalum, as the author will subsequently show that the amount of oxygen in the acid is much greater than that established by Berzelius.

If chlorine gas be passed over metallic tantalum, no action takes place at ordinary temperatures; but with a gentle heat the metal glows in the chlorine gas, and may be distilled in the form of chloride of tantalum, whilst a considerable quantity of acid tantalate of soda often remains, constituting the impurity of the metal. Of this a small portion is converted into chloride of sodium by the action of the chlorine.

Metallic tantalum may be reduced from tantalic acid by passing vapours of phosphorus over tantalate of soda heated to redness. The salt becomes quite black; and when the black mass is treated with water after cooling, phosphate of soda is dissolved. But this tantalum, notwithstanding its very black colour, is contaminated with a great deal of bitantalate of soda, so that it only contains about 6 to 7 per cent. of pure metal, and is therefore a non-conductor of electricity.

When tantalic acid or chloride of tantalum is treated at a high temperature with ammoniacal gas, metallic tantalum is not obtained, but, as the author will hereafter show more clearly, nitrogenous compounds.

As regards the preparation of perchloride of tantalum, the author has already spoken fully in previous memoirs, and also mentioned, that in preparing it by means of chlorine gas from a mixture of tantalic acid and charcoal, the formation of fluid chloride of tin is also frequently observed, when the tantalic acid has not been previously purified from oxide of tin with the utmost care; this can only be effected by fusion with a mixture of sulphur and carbonate of soda, and not by mere digestion with sulphuret of ammonium.

The analyses of perchloride of tantalum did not give such concordant results as would have been desirable to enable the atomic weight of tantalum to be determined with greater certainty. There are many circumstances which stand in the way of great accuracy. Volatile chlorides of the solid state of aggregation, especially when they are of a voluminous nature and do not readily crystallize, never furnish such exact results in the investigation of their composition as the volatile fluid chlorides or solid chlorides of a distinctly crystalline nature. On the one hand, they often contain very small quantities of chlorine in excess, which can only be got rid of with difficulty by long passage of a current of atmospheric air at the ordinary temperature; and on the other hand, some oxychloride.

The author does not take the average of all his experiments, but only that of the few which have the greatest probability of correctness. From these he supposes that perchloride of tantalum consists of—

Tantalum	49·25
Chlorine	50·75

The composition of tantalic acid is therefore—

Tantalum	81·14
Oxygen	18·86

This determination, however, differs greatly from that of Berzelius, according to which the composition of tantalic acid is—

Tantalum	88·49
Oxygen	11·51

Berzelius determined the composition of tantalic acid from that of sulphuret of tantalum. The author will hereafter show in his investigations of sulphuret of tantalum, that Berzelius was mistaken in his conclusions, whilst his experiments perfectly agree with those of the author.

With regard to the atomic constitution of tantalic acid, the author was long unable to come to any conclusion. Berzelius supposed that it contained 3 atoms of oxygen to 2 atoms of metal; but for several reasons, developed by the author in his memoir, he considers himself justified in regarding tantalic acid as composed of 2 atoms of oxygen to 1 atom of metal, by which the composition of most of the compounds may be very satisfactorily explained. The atomic weight of tantalum will thus be 860·26.

Perbromide of tantalum is obtained in the same way as the perchloride. It is yellowish, but only when it is freed from the excess of bromine, which gives it a more brown colour. This is effected with difficulty.

A periodide of tantalum could not be prepared in the same way as the perchloride and perbromide. It could not be prepared even by fusing iodine with metallic tantalum.—*Bericht der Akad. der Wiss. zu Berlin,* 1856, p. 385.

Upon Hyposulphate of Copper and Ammonia. By E. SCHWEIZER.

Heeren obtained the hyposulphate of copper and ammonia by mixing a solution of hyposulphate of copper with ammonia until the precipitate at first produced was again dissolved. As the compound is soluble with difficulty, it soon crystallizes. The author prepares the same salt by precipitation from sulphate of copper and ammonia, $2NH^3, CuO, HO+SO^3$, by means of hyposulphate of baryta. The compound has exactly the formula established for it by Heeren $=2NH^3, CuO+S^2O^5$; it contains no water, crystallizes in thin prisms with oblique terminal faces, possesses a splendid violet colour, and is stable in the air. In cold water it is difficult of solution, but dissolves pretty readily in water about 104° F. In the absence of free ammonia it is decomposed by much water, giving rise to the formation of a bluish precipitate. A decomposition takes place also when the solution is heated. This commences as low as about 140° F., but is also prevented by the presence of free ammonia. Analyses:—

NH^3	23·16	22·97	2 =	34·00	23·34
CuO	27·65	27·61	1	39·68	27·21
S^2O^5	49·19	49·42	1	72·00	49·45

Muriatic acid decomposes the salt. When dilute muriatic acid is dropped into a solution of the salt, a precipitate is produced, and all at once the fluid is completely decolorized. If no excess of muriatic acid be added at this moment, the filtered fluid contains hyposulphate and muriate of ammonia with, at the utmost, traces of oxide of copper. The precipitate contains chlorine, oxide of copper and water, and is probably a mixture of Brunswick-green with hydrated oxide of copper. Its analysis gave—

CuCl	24·22	2 =	134·36
CuO	56·26	7	277·76
HO	16·52	9	81·00

Water decomposes the salt. If a solution, slightly heated, be poured into a large quantity of water, a blue precipitate is produced and the fluid becomes nearly colourless. The decomposition consists in the formation of hydrated oxide of copper, hyposulphate of ammonia and water.

Heat.—By heating the solution to 140° F., and still more by boiling it, the hyposulphate of copper and ammonia is decomposed. A precipitate of oxide of copper with some hyposulphate of copper is formed.

The dry salt only undergoes alteration at 320° F., when it acquires a dark green colour, without losing its form and lustre. A portion of the ammonia is driven off, whilst a portion of the hyposulphuric acid is oxidized into sulphuric acid.

The author regards the hyposulphate of copper and ammonia as a conjugated compound of oxide of copper with ammonia, $CuO\frown 2NH^3$, with hyposulphuric acid, according to which its formula is $(CuO\frown 2NH^3)\,S^2O^5$.—*Journ. für Prakt. Chem.*, lxvii. p. 430.

On the supposed Identity of Oxyphenic Acid with colourless Hydrochinone. By R. Wagner.

Against the opinion that colourless hydrochinone and oxyphenic acid are identical, the author observes,—1st, that oxyphenic acid sublimes without alteration; 2ndly, that in the air it is converted by solution of potash into a black humus-like substance, even in a few minutes; 3rdly, that it is destroyed by hypochlorous acid, and furnishes no green hydrochinone; 4thly, that it is completely decomposed by nitrate of silver and chromate of potash. In these respects it differs from colourless hydrochinone. The lead-salt of oxyphenic acid is $C^{12}H^4Pb^2O^4$, that of hydrochinone is $C^{12}H^6O^4$, $2C^4H^3PbO^4+3HO$.—*Journ. für Prakt. Chem.*, lxvii. p. 490.

Contributions towards the Knowledge of the Salts of Lithia.

By C. Scheibler.

The author has prepared the following salts of lithia in Werther's laboratory.

Platinochloride of Lithium, $LiCl+PtCl^2+6HO$, crystallizes from a mixture of the two chlorides in large, orange-red, broad laminæ; it effloresces, and then becomes dull yellow. It is insoluble in æther; soluble in water, alcohol, and æther and alcohol; and behaves towards reagents, and when calcined, in the same way as the corresponding soda-salt. Analysis:—

Li	2·67	1	=	6·5
Pt	36·64	1		99·0
Cl	..	3		106·5
HO	19·81	6		54·0

Racemate of Antimony and Lithia, $(LiO+SbO^3)C^8H^4O^{10}+5HO$.—Oxide of antimony, precipitated by ammonia from tartrate of antimony and well washed, was treated with a boiling solution of biracemate of lithia, and the filtrate separated from the excess of oxide of antimony brought to crystallize. It forms brightly shining needles, growing out in tufts from a single point, which are obtained in larger, beautiful, well-developed, rhombic prisms, with the apices of the octahedron, by slow evaporation. It is stable in the air, and behaves exactly like tartar emetic.

Biracemate of Lithia is a strongly efflorescent salt, without any remarkable characters.

Acetate of Uranium and Lithia, $(LiO, 2Ur^2O^3)\,3(C^4H^3O^3)+6HO$, is obtained in beautiful large crystals by mixing equal equivalents of the simple salts and leaving them to evaporate in the air. The fresh crystals have a beautiful lustre and the dichroism of the other uranium-salts. Analysis:—

LiO	61·15	1	=	14·5	59·21
Ur^2O^3		2		286·0	
$C^4H^3O^3$	..	3		153·0	30·15
HO	9·73	6		54·0	10·64

Butyrate of Lithia, $LiO, C^8H^7O^3+HO$, prepared with carbonate of lithia, crystallizes from the syrupous solution in inconspicuous laminar crystals, which effloresce strongly and creep up over the edge of the vessel. It is very difficult of solution in alcohol, and insoluble in æther; it fuses when heated, giving off HO and forming a clear fluid, and afterwards becomes decomposed, with formation of products of a very agreeable odour and combustible gases, leaving carbonate of lithia. Analysis:—

LiO	14·05	1	=	14·5	14·14
$C^8H^7O^3$	..	1		79·0	77·07
HO	9·40	1		9·0	8·78

Valerianate of Lithia, $LiO, C^{10}H^9O^3+2HO$, crystallizes from the syrupous solution in globular verrucous masses. Analysis:—

LiO	11·52	1 =	14·5	11·55
$C^{10}H^9O^3$	..	1	93·0	74·10
HO	14·43	2	18·0	14·34

Succinate of Lithia, $2LiO, C^8H^4O^6$, forms beautiful, transparent, glassy crystals, often ½ an inch in diameter, which are anhydrous, decrepitate strongly when heated, and with a higher temperature become decomposed, with evolution of empyreumatic products, leaving carbonate of lithia. It is insoluble in alcohol and æther, but readily soluble in water. Analysis:—

LiO	22·48	2 =	29	22·48
$C^8H^4O^6$	..	1	100	77·52

Lactate of Lithia, $C^{12}H^{10}O^{10}, 2LiO+3HO$, forms crystals with a fatty lustre, grouped in a verrucose form round a point. It is completely insoluble in alcohol and æther, but readily soluble in water. At 212° F. the salt loses its water of crystallization; when more strongly heated, it fuses and becomes decomposed at the same time, becoming strongly inflated, evolving empyreumatic products, and leaving carbonate of lithia containing carbon. Analysis:—

LiO	12·72	2 =	29	13·30
$C^{12}H^{10}O^{10}$	..	1	162	74·31
HO	11·96	3	27	12·39

Double sulphates of lithia with the bases of the magnesia series, namely MnO, FeO, NiO, CuO, ZnO, could not be prepared.—*Journ. für Prakt. Chem.*, lxvii. p. 485.

On some Salts of Oxaminic Acid. By P. J. Engström.

As the formation of oxaminic acid essentially depends upon the separation of water from an acid ammoniacal salt, the author was led to prepare oxaminate of potash by heating the neutral double oxalate of potash and ammonia. If crystals of this salt be kept at 446° F., with replacement of the evaporated ammonia, until the salt has lost its fluid form, the residue dissolves entirely in water with a slight brown colour when the conversion has been complete. From the solution, if not too dilute, chloride of barium precipitates a powder with a nearly golden-yellow colour, which dissolves completely in boiling water. If the oxalic acid be not completely transformed, which may easily occur in the preparation of large quantities, oxalate of baryta is left undissolved. In this way therefore we prepare oxaminate of baryta, which then furnishes the corresponding oxaminates with the sulphates of other bases.

Oxaminate of Potash, $NH^2, C^2O^2 \frown KO\,C^2O^3 + 2HO = KO, C^4H^2NO^5+2HO$.—Silky needles, readily soluble in water, less so in alcohol. It loses nothing over sulphuric acid; at 212° F. it loses

12·34 per cent. of water, and nothing more at 392° F. The air-dried salt contained 30·83 per cent. of potash:—

KO	30·83	1	30·48
HO	12·34	2	12·40

Oxaminate of Soda, $NH^2 C^2 O^2 \frown NaO, C^2 O^3 + HO = NaO, C^4 H^2 NO^5 + HO$.—Four-sided microscopic needles, which effloresce readily. Air-dried, it loses 7·52 per cent. of water at 212° F., and contains 26·31 of soda. Crystallized from a hot solution, it only contains 2·38 to 2·33 per cent. of water, corresponding with the formula $2(NaO, C^4 H^2 NO^5) + 3HO$.

Oxaminate of Ammonia, $NH^4 O, C^4 H^2 NO^5$, forms readily soluble four-sided prisms when it crystallizes from a hot solution, and small grains when it separates from a cold solution. The prisms are anhydrous, as Balard has already stated; they lose ammonia at 212° F., give a white sublimate, and leave behind a very soluble, somewhat yellowish salt.

The Granular Salt is $NH^4 O, C^4 H^2 NO^5 + 3HO$.—It does not effloresce, and contains 20·63 to 20·11 per cent. of water. A salt with 2 equivs. of water also appears to exist.

Oxaminate of Baryta, $BaO, C^4 H^2 NO^5 + 3HO$.—The salt prepared by the author's process is yellow, but becomes perfectly white, like Balard's preparation, by treatment with animal charcoal. The anhydrous salt requires 537 parts of water at 55°·4 F., and 25·6 parts at 212° F. for its solution. The analysis of the hydrated salt gave,—

BaO	41·693	42·587
HO	14·69	15·8
N	7·24	

Oxaminate of Lime, $CaO, C^4 H^2 NO^5 + 4HO$.—This is best obtained by the precipitation of a solution of chloride of calcium with oxaminate of ammonia. It is stable in the air, loses 24·47 per cent. of water at 212° F., and 0·74 per cent. more at 392° F. It contains,—

CaO	19·38	1	19·44
HO	25·21	1	25·00

1 part of the anhydrous lime-salt requires 638 parts of water at 55°·4 F. and 24·6 parts at 212° F. for its solution.

Oxaminate of Magnesia, $MgO, C^4 H^2 NO^5 + 3HO$, separates on the evaporation of its solution in small granules, which consist of extremely slender grouped needles. It lost 3·5 per cent. of water in a current of dry air, and 20·74 to 21·21 per cent. at 212° F., corresponding with the above formula. Analysis:—

MgO	15·88	..	1	15·91
HO	20·74	21·21	1	22·22

Ofversigt af Kongl. Vet. Akad. förhandlingar, 1855, p. 305.

On the Compounds of Phosphomolybdic Acid with some Bases.

By Dr. Max Seligsohn.

The author has made an investigation of the compounds formed by phosphomolybdic acid, in the laboratory of Dr. Sonnenschein of

Berlin. Svanberg and Struve have expressed the opinion, that molybdic acid is converted into an allotropic state by a small quantity of phosphoric acid. Sonnenschein, on the contrary, stated that the amount of phosphoric acid in the molybdic acid could be obtained constant. The author has prepared the following compounds of phosphomolybdic acid.

Phosphomolybdate of Ammonia, $2(3NH^4O + PO^5) + 15(HO + 4MoO^3)$.—The crude molybdic acid obtained by fusing native molybdate of lead with carbonate of soda, lixiviation with water containing a little nitric acid, and supersaturation with muriatic acid, is mixed with solution of muriate of ammonia. The solution is filtered and mixed with phosphate of soda. The yellow precipitate, collected, dried at 212° F., and analysed, gave,—

MoO^3	90·744
PO^5	3·142
NH^4O	3·570
HO	2·544

These results do not agree with those published by Nutzinger in Wittstein's 'Vierteljahrschrift,' iv. p. 549. This salt, the yellow precipitate, served for the preparation of the following salts:—

Soda-salt, $2(3NH^4O + PO^5) + 15(NaO, 4MoO^3 + 18HO)$.—The yellow precipitate dissolves in an excess of a dilute solution of acetate of soda. When evaporated to a certain degree of concentration, a magma of shining crystals is produced, which are washed with alcohol. The dried crystalline mass appears under the microscope as an aggregation of fine asbestos-like needles, the crystalline form of which could not be more exactly determined. It is insoluble in alcohol, soluble in an excess of boiling water, to which it then communicates an acid reaction. If acids be poured over the salt, the yellow precipitate immediately separates, especially on the application of heat. At a red heat the salt fuses, and solidifies on cooling in a crystalline form, with a yellow colour. Analysis:—

MoO^3	82·39	..	60	81·940
PO^5	2·865	2·608	2	2·786
NaO	9·577	9·320	15	9·228
NH^4O	..	..	6	3·040
HO	6·20	6·35	8	3·006

This salt has given origin to the formula previously established for the yellow precipitate, for the water in the latter appears here to be replaced by an equal number of equivalents of soda.

Potash-salt, $2(3NH^4O + PO^5) + 15(KO, 4MoO^3)$, obtained by means of acetate of potash, but otherwise in the same way as the preceding salt, is less crystalline, fuses when heated to redness, and solidifies in a crystalline form on cooling. When treated with acids, it immediately yields a precipitate, especially when the action takes place with the assistance of heat. Analysis:—

MoO^3	79·380	4·83 . 5·09	60 =	52500·00	79·04
PO^5	2·846		2	1784·08	2·68
KO	13·456		15	8832·90	13·28
NH^4O	2·711	4·83 . 5·09	6	1950·36	2·95
HO	..		2	1350·00	2·05

Baryta-salt, $30(BaO, MoO^3)+(3NH^4O+PO^5)$, prepared by means of acetate of baryta in the same way as the preceding salt. It separates in the form of a white powder, which lets fall the yellow precipitate on the addition of acids. This salt has the same composition as that which Svanberg and Struve obtained by treating an ammoniacal solution of the yellow precipitate with chloride of barium. When dried at 212° F., it gave,—

			Calculated.	In 100 parts.	Svanberg and Struve found in 100 parts.
MoO^3	46·518	30 =	26250·00	46·175	46·769
BaO	50·460	30	28719·60	50·505	50·543
PO^5	1·360	1	892·04	1·570	1·087
NH^4O	1·662	3	975·18	1·750	1·601

Lead-salt, $30(MoO^3, PbO)+(3NH^4O+PO^5)$, obtained by means of acetate of lead with exclusion of air, in the same way as the preceding. It forms a white powder, which behaves towards acids in the same way as the preceding salts. Analysis of the salt, dried at 212° F.:—

MoO^3	37·231	36·765	30 =	26250·00	37·553
PbO	60·068	60·480	30	41839·50	59·794
PO^5	1·450	1·328	1	892·04	1·260
NH^4O	1·251	1·427	3	975·18	1·393

Arseniomolybdate of Ammonia, probably $(3NH^4O+AsO^5)+6(HO, 4MoO^3)$, is obtained when nitric acid is added at a boiling heat to an ammoniacal solution containing some arseniate of soda and an excess of molybdic acid. The yellow precipitate, containing arsenic acid, molybdic acid and ammonia, immediately separates. Analysis:—

MoO^3	87·666		24 =	21000·00	87·182
AsO^5	6·308		1	1437·50	5·970
NH^4O	4·258	5·837 . 6·02	3	975·18	4·048
HO	..		6	675·00	2·800

Phosphomolybdate of Æthylamine, $2([C^4H^7N, HO]^3+PO^5)+15(HO, 4MoO^3+9HO)$, is the yellow precipitate formed when a solution of æthylamine in muriatic acid is added to an acid solution of phosphomolybdic acid. It only differs from the corresponding ammoniacal precipitate by its somewhat paler colour. Analysis of the salt, dried at 212° F.:—

MoO^3	85·283	85·496	30 =	26250·00	85·689
PO^5	3·256	3·022	1	892·04	2·932
C^4H^7N, HO	11·234	6·965	3	2025·18	6·635
HO		..	12	1350·00	4·753

Phosphomolybdate of Triæthylamine is produced when a solution of triæthylamine in muriatic acid is added to a solution of phosphomolybdic acid. Analysis;—

Molybdic acid............	79·040	78·85	
Phosphoric acid	3·050	2·82	
Triæthylamine and water ..	..	..	18·54

Journ. für Prakt. Chem., lxvii. p. 470.

On some Compounds of Cyanogen with the Alkaline Earths.
By Dr. C. Schulz.

Cyanide of Barium.—When hot solutions of 2 parts of ferrocyanide of potassium and 1 part of chloride of barium are mixed together, the double salt $2KCy, FeCy+2BaCy, FeCy+6HO$ is obtained. This is deprived of water at 212° F., and calcined at a gentle red heat, with exclusion of air. The residue is powdered, lixiviated with water, and the solution decanted from the carburet of iron. The solution contains cyanides of potassium and barium. The fluid is distilled; ammonia passes as a product of decomposition of the cyanide of potassium, and the residue is set to crystallize. Crystals of pure cyanide of barium, free from potash, are obtained; they are difficult of solution in water, and when exposed to the air quickly cover themselves with a coat of carbonate of baryta. The salt dissolves readily in water containing cyanide of potassium, probably in consequence of the formation of a double salt. The solution of cyanide of barium may be boiled without decomposition in the absence of air.

Cyanide of Strontium is obtained in exactly the same way from ferrocyanide of potassium and strontium, prepared by boiling prussian blue with strontian water, evaporating it and depriving it of its water at 212° F. It forms crystals exactly like those of cyanide of barium, which are rapidly decomposed in the air, especially in solution.

Cyanide of Calcium was also prepared in the solid form from the ferrocyanide of calcium, which is thrown down by mixing a concentrated solution of chloride of calcium with ferrocyanide of potassium. When its solution is concentrated by boiling in a retort, cyanide of calcium crystallizes in cubes, and behaves like the preceding salts; it does not however appear to be decomposed so rapidly as cyanide of barium by the carbonic acid of the air.

Cyanide of Magnesium was prepared from the yellowish precipitate of ferrocyanide of potassium and magnesium, which is thrown down by mixing sulphate of magnesia and ferrocyanide of potassium. The solid salt, the crystals of which are very similar to those of the calcium compound, behaves like the preceding salts, but is the most stable of all in the air, as it is less readily decomposed by carbonic acid.

Double compounds of ferrocyanide of copper with the ferrocyanides of potassium, sodium and ammonium, are obtained in the following way:—

Ferrocyanide of Copper and Potassium, $(Cu^2Cy)^2, FeCy+(KCy)^2, FeCy+3HO$, is obtained when the reddish-brown precipitate of $2CuCy+FeCy$, produced by ferrocyanide of potassium in per-salts of copper, is dissolved in a solution of cyanide of potassium, and heated. A strong evolution of cyanogen gas takes place, the solution becomes yellow, and soon deposits a reddish-brown precipitate, which is separated by filtration. After long standing, small, dark, brownish-red crystals make their appearance in the filtrate, which are shown by the microscope to be quadratic prisms. The deposition of the reddish-brown precipitate may be avoided, if an excess of cyanide of potassium be added to the solution.

These crystals are more conveniently obtained by slowly dropping solution of sulphate of copper into a mixture of cyanide and ferrocyanide of potassium; the precipitate of $2CuCy, FeCy+2KCy, FeCy$, which is at first produced, dissolves again in the excess of cyanide of potassium on the application of heat; and on cooling, if there was not sufficient cyanide of potassium, a portion of the ferridcyanide of copper compound separates again on cooling. If cyanide of potassium be present in sufficient quantity, a solution of the protocyanide compound alone is formed; and this, when left standing for a long time, furnishes crystals of this salt.

These crystals lose water, and become black at 212° F. They are insoluble in water, æther and alcohol, but dissolve in solution of cyanide of potassium. Boiling water dissolves a little of them, with partial decomposition, by which ferrocyanide of potassium is formed. Acids decompose the salt partially, with formation of white protocyanide of copper and iron, $2Cu^2 Cy+FeCy$, which is immediately oxidized by exposure to the air into $2CuCy, FeCy$.

The compound $(CuCy)^2, FeCy + (KCy)^2, FeCy + 2HO$, is the reddish-brown precipitate deposited in the preparation of the preceding salt when a smaller quantity of cyanide of potassium is employed. It dissolves in a solution of cyanide of potassium, with evolution of cyanogen.

Cyanide of Sodium, when treated in the same way with ferrocyanide of copper, furnishes the corresponding sodium compounds—

$$(Cu^2 Cy)^2, FeCy+(NaCy)^2, FeCy,$$
$$(Cu\ Cy)^2, FeCy+(NaCy)^2, FeCy.$$

Cyanide of Ammonium also furnishes a compound belonging to the same series as the above bodies. Ferrocyanide of copper dissolves with some difficulty in a solution of cyanide of ammonium. On the evaporation of the slightly yellowish fluid, a scarlet crystalline body separates, which becomes darker on drying. It is the compound—

$$(CuCy)^2, FeCy+(NH^4\ Cy)^2, FeCy,$$

which is exactly similar to the corresponding potassium and sodium compounds.

Similar compounds are obtained when the ferrocyanides of cobalt and nickel are treated with cyanide of potassium.

A compound of protopercyanide of copper with protocyanide of iron, analogous to prussian blue, is obtained by dissolving 3 equivs. of sulphate of copper and 1 equiv. of sulphate of iron in water, diluting it greatly, and adding ferrocyanide of potassium in such quantity that a portion of the salt remains undecomposed, so that the fluid continues bluish after filtration.

A deep black precipitate is obtained, which remains unchanged in the air. When dry it forms deep black, very shining fragments, which when triturated furnish a black powder. It shows no trace of crystallization. When heated, it first gives off water; when submitted to dry distillation at a higher temperature, it begins to decompose at 266° F., and furnishes a sublimate of cyanide of ammonium and carbonate of ammonia, with a constant elimination of water and evolution of nitrogen and cyanogen gases; the residue contains copper, iron and carbon.

When heated with access of air, this body exhibits the usual smouldering, and burns, with evolution of hydrocyanic acid and cyanogen gas, to a mixture of peroxide of iron and copper and protoxide of copper. The formation of the latter was entirely dependent on the temperature and the access of air.

It is insoluble in water, alcohol and æther. When boiled with water, it is partially decomposed, hydrocyanic acid is evolved, and metallic copper separates. Dilute sulphuric, muriatic, and nitric acids leave it unaltered. With concentrated sulphuric acid it forms a white pasty mass, which dissolves in an excess of acid. The same black body is separated unchanged from this solution by the addition of water, a behaviour which is exhibited by many cyanides, as for instance prussian blue. Concentrated muriatic and nitric acids decompose the fresh precipitate very energetically—the dried one with less ease. A pale green precipitate is formed, and the supernatant fluid is coloured blue by dissolved persalts of copper.

If the black precipitate be diffused in water, and a current of chlorine passed through it, a pale green precipitate is also produced. The fluid filtered therefrom contains dissolved perchloride of copper, whilst evolved chloride of cyanogen is recognizable by its odour. If the precipitate be suspended in water, and a current of sulphuretted hydrogen be passed through the fluid, sulphuret of copper is produced. The filtrate smelled strongly of hydrocyanic acid, and acquired a blue colour by exposure to the air. It therefore contained hydroferrocyanic acid, which was again decomposed.

Solution of potash decomposed the fresh precipitate very readily, the dried one with less ease. Ferrocyanide of potassium was dissolved, and the residue proved to be a mixture of protoxide and peroxide of copper. A solution of oxalic acid dissolves the precipitate unchanged.

From the inalterability with oxalic acid, it appears that no prussian blue could be present, but that the precipitate must be a determinate compound; and from the behaviour with potash, it follows that this body is a compound of protocyanide of iron with protocyanide and percyanide of copper, and this is confirmed by analysis, which led to the formula above given.—*Journ. für Prakt. Chem.*, lxviii. p. 257.

Trimethylamine obtained from the Human Urine.
By M. Dessaignes.

Having had to evaporate large quantities of urine in the preparation of creatine, I was struck by the peculiar odour presented by the carbonate of ammonia which is disengaged from this liquid when concentrated and boiling, and I endeavoured to isolate the body to which this odour might belong. With this view I distilled the urine, and saturated the product of the distillation with muriatic acid. The liquid, which smells strongly of ammonia, also presents an odour of putrid fish, which becomes especially sensible when neutralization is approached. When acid is added in slight excess, it acquires a reddish colour; this is due to one of the volatile acids detected in the urine by M. Städeler. I separated large quantities of muriate of ammonia by crystallization. The mother-liquor was evaporated to dryness and the residue taken up by absolute alcohol, and I then added chloride of platinum to the alcoholic solution. After several crystallizations I obtained superb crystals, which presented exactly the form of the platinum-salts prepared with the *Chenopodium vulvaria*, and which is the chloroplatinate, not of propylamine, as I supposed at the time, but of trimethylamine. Such is also the composition of the salt obtained from urine, as is proved by the following numbers:—

	Calculated.	Found.
C^6	13·58	13·85
H^{10}	3·77	3·94
N^2	5·26	5·32
Cl^6	40·22	40·23
Pt	37·17	37·02

Trimethylamine accompanies the ammonia which is evolved from boiling urine in very small quantity. Thus 65 litres of liquid obtained by the distillation of urine previously concentrated, furnished 2·200 grms. of muriate of ammonia, and only 17 grms. of chloroplatinate of trimethylamine, corresponding to 3·7 grms. of free alkali.

In the mother-liquors of the platinum-salt I obtained some crystals of the same form as those of trimethylamine, but much smaller. When calcined, they left 41·40 per cent. of platinum, and evolved an odour of putrid fish. From these characters it is easy to recognize the chloroplatinate of methylamine.

Does trimethylamine pre-exist in the urine? Is it not rather, like ammonia, the product of the decomposition of another body by heat and the action of the mineral salts present? Is it formed in greater abundance by the putrefaction of the urine, as it is developed in the flesh of putrescent fishes? I leave these questions undecided at present.—*Comptes Rendus*, Sept. 29, 1856, p. 670.

On an Alloy of Lead and Iron produced in a Blast-Furnace.

By F. L. SONNENSCHEIN.

During the last period of the working of the blast-furnace at the "Marienhütte" in Upper Silesia, where brown ironstone is smelted, a remarkably large amount of lead was observed. Thus when the furnace had been in operation about five years, lead ate through under the hearth sideways about 6 inches below the tapping hole, so that with every tapping of iron, lead was contained in the iron. In consequence of this a small cavity was formed below the tapping hole after every tapping, in which the lead collected, and which was emptied several times in the twenty-four hours. The amount of lead increased in such a way that in the last eighteen months 526 cwts. of 2½ to 3 oz. assay lead was obtained in this manner. After being seven years in operation, the furnace was blown down. On breaking it up, the pigs which had formed in the channels exhibited not only much lead, but also various aggregations of crystals, of which some were regarded as titaniferous iron from their external appearance. Besides, red crystalline groups were found in the eroded masses. The crystals resembling titaniferous iron which were found in the cavities of the pigs formed partly cubes, which were here and there placed upon each other like steps; but the greater part of them consisted of acicular crystals grouped in a plumose form. The colour was principally brassy yellow, but passed in particular places into a peculiar glittering blue. They were soft, rather harder than lead, but could be easily cut, forming a cut surface with a leaden lustre. They were strongly attracted by the magnet. Spec. grav.=10·560.

From several analyses performed by Nauwerk and Wersky in the author's laboratory, these crystals consist of 88·76 lead and 11·14 iron, corresponding to a compound of 1 atom iron and 2 atoms lead, which from calculation would consist of 88·08 lead and 11·92 iron. Such a compound has hitherto never been observed, and is the more remarkable as lead has very little affinity for iron, so that when the two are fused together, two compounds in strata one above the other are obtained, of which the lower contains very little iron and the upper very little lead. By the reduction of a slag containing lead and iron, Biewend prepared a well-fused, hard, almost entirely brittle, pale steel-gray, shining, metallic alloy, with a finely granular laminar fracture, containing 96·76 of iron and 3·24 of lead.

The formation of the extremely interesting alloy above described may perhaps be explained by the long action of gaseous lead upon metallic iron.

The red crystalline groups above mentioned are partly surrounded by minium. They form cubes and varieties of cubes, have a glassy lustre, and consist of pure lead, the surface of which is coated with an extraordinarily thin layer of red oxide,—*Zeitschr. der Deutsch. Geolog. Gesellsch.*, vii. p. 664.

ANALYTICAL CHEMISTRY.

Upon a new Method of determining Phosphoric Acid.

By Dr. W. Knop.

The properties of some salts of oxide of uranium, which were known to me from having once occupied myself in Wöhler's laboratory with pitchblende, led me to the idea of employing acetate of uranium for the qualitative and quantitative determination of phosphoric acid.

If a substance containing phosphoric acid be dissolved in some acid, as for example muriatic or nitric acid, and ammonia be then added to it until this is present in excess, this fluid be supersaturated with acetic acid and heated to boiling, the addition of every drop of the solution of acetate of uranium produces a yellowish-white cloud of phosphate of uranium and ammonia, a new salt which is perfectly insoluble in free acetic acid.

The solution of acetate of uranium however most remarkably decomposes all the phosphates of potash, soda, ammonia, baryta, lime, magnesia, alumina and oxide of iron. If we have a fluid containing all these bodies in acid solution, supersaturate it with ammonia until a precipitate is produced, then add some acetate of ammonia and much free acetic acid, heat it to boiling, and mix the boiling fluid with an excess of acetate of uranium, all these bases pass into solution free from phosphoric acid, whilst the phosporic acid itself is precipitated in the form of phosphate of uranium and ammonia.

By means of this method I have completely decomposed phosphate of iron and analysed pure phosphate of alumina, and obtained perfectly exact results. From a further examination of the behaviour of oxide of uranium under the above-mentioned circumstances, it appears,—

1. That acetate of uranium is the most exact qualitative reagent for phosphoric acid; I regard it as more exact than the test with molybdic acid.

2. That in the presence of an abundance of ammonia, phosphoric acid is always thrown down as $(Ur^2 O^3)^2, NH^4 O, PO^5$, a salt similar to the phosphate of ammonia and magnesia, which when calcined leaves $Ur^4 O^6, PO^5$ of the atomic weight 357. Exactly one-fifth of this (20 per cent.) is phosphoric acid.

3. That in the acetate of uranium we have a means of entirely getting rid of phosphoric acid from analysis.

The method of determining phosphoric acid, which I hereby recommend to chemists, has certain advantages over those hitherto known. By the assistance of M. Arendt, I have already been able to carry out a series of analyses, which will be communicated on a future occasion, in order to prove the applicability of my method to analyses of ashes, urine, minerals, &c.—*Chemisches Centralblatt*, No. 47, Oct. 8 ,1856, p. 737.

On Compounds of Oxide of Bismuth with Chromic Acid; the Quantitative Determination of Oxide of Bismuth, and its Separation from Oxide of Cadmium. By Dr. J. Löwe.

A moderately concentrated solution of bichromate of potash, with a solution of pernitrate of bismuth containing as little free acid as possible, taking the precaution of pouring the solution of bismuth into that of the chromate, gives a yellow flocculent precipitate, which afterwards assumes a crystalline form, and becomes very dense, heavy and granular. With the assistance of heat, the precipitate is obtained at once in the latter form. It is insoluble in boiling and cold water, and may be dried at 212° to 257° F. without decomposition; but when heated to redness it becomes blackish-green, whilst its original colour does not return on cooling. Nitric and muriatic acids dissolve the yellow salt without difficulty, more readily in the dilute than in the concentrated state; the solution has a dark yellow colour, and becomes turbid on the addition of water by the separation of basic pernitrate or chloride of bismuth.

The salt has constantly the composition $BiO^3,2CrO^3$, and contains 30·301 per cent. of chromic acid and 69·477 of peroxide of bismuth, BiO^3.

From its insolubility this salt is adapted for quantitative determination; the method with carbonate of ammonia is to be preferred; and as chromate of cadmium is soluble, it may also serve for the separation of bismuth from cadmium.—*Journ. für Prakt. Chem.*, lxvii. p. 463.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of chemically pure Sulphuric Acid. By F. Vorwerk.

Some time ago Russegger described a method in which, by a particular arrangement of the retorts, sulphuric acid may be distilled by boiling without thumping, and the rectification of the crude acid may be effected without the employment of platinum wire. Instead of this the author recommends the following process, which fulfils the same purpose, and dispenses with all further particular arrangements.

Into a long-necked plain retort, which had already served several times for the preparation of nitric acid, 5 lbs. of slightly brown English sulphuric acid, of spec. grav. 1·832 and free from arsenic, were put. The retort was put upon a layer of sand of the depth of a finger in the sand-bath, and surrounded with sand, so that it was buried up to the neck. A long-necked flask served as a receiver; it was simply pushed over the neck of the retort without any luting. Commencing with a moderate heat, this was gradually raised until the sand-bath became red-hot, during which the distillation went on quite regularly without any thumping. Notwithstanding the heat to which the retort was exposed, the receiver did not require to be cooled until after six hours' working, and even then only by wrapping a wet cloth round the neck. The distillate was removed from time to time, and tested as to its purity and specific gravity. The first 5 oz. that passed had a specific gravity of 1·20, and exhibited no impurity except a considerable quantity of sulphurous acid. The second portion of 3½ oz. of distillate, with a specific gravity of 1·75, still contained a trace of sulphurous acid. A third portion of 2½ oz. was pure, and had a specific gravity of 1·850.

Fourth portion of	1½ lb.	spec. grav. 1·855
Fifth portion of	13 oz.	spec. grav. 1·860
Sixth portion of	9 oz.	spec. grav. 1·885

With this the distillation was concluded, to enable the contents of the retort to be examined. The uninjured retort contained the remainder of the sulphuric acid as a limpid fluid with a white sediment (persulphate of iron), from which no doubt ½ lb. of pure distillate might still have been obtained.

In such distillations, particular attention is to be paid to the quality of the retort. It is always advisable to anneal the retort before using it, by heating it as strongly as possible in the sand-bath, and letting it cool slowly and completely therein.—*Neues Jahrbuch für Pharm.*, v. p. 257.

On the Preparation of Drying Oil. By Prof. R. Wagner.

The author repeatedly prepared protoborate of manganese for lacquerers, in accordance with the directions of Barruel and Jean. He effected its precipitation whilst hot, and thus obtained it of a coffee-brown colour, and consequently containing much oxide, but still always of remarkable efficacy. As, however, Barruel and Jean expressly observe that the action is proper to the protosalts, the author endeavoured to obtain it perfectly free from oxide, and for this purpose effected the precipitation with borax cold. He obtained a snow-white powder, but this furnished no varnish. He therefore returned to the previous mode of preparation with the assistance of heat, and found that it was obtained of the darkest brown, and also of the strongest action, when both the solutions of sulphate of manganese and borax were diluted as much as possible and mixed boiling. The siccative action upon the oil must therefore be ascribed to the oxide, and not to the protoxide.

By further experiments the author found that the boracic acid is quite superfluous, and that free oxide of manganese or its hydrate is as efficacious as the borate. The oil need only be heated for a very short time (about a quarter of an hour) with about one-eighth per cent. of oxide or hydrated oxide of manganese. The heat applied need not approach the boiling-point by a long way; but no general temperature can be given, as new oil has a much higher boiling-point than old. The siccative quality however increases with the heat. But as the oil becomes darker and thicker in proportion to the heat to which it is exposed, it is the best plan in general to remove it from the fire as soon as it clears and begins to fume very slightly. Streaks of it now become firm in twenty-four hours. To obtain the drying oil of a very pale colour, it must be heated still less. The drying is thus retarded several hours, but the colour has scarcely become perceptibly brownish, whilst in the former case it always acquires a chestnut-brown colour.

The author obtained a wine-yellow oil, quite unaltered, without heat, by mixing 1 per cent. of hydrated lime with a linseed-oil four years old, which dried by itself in three days. After being frequently stirred for two days, a streak of it was perfectly firm in twenty-four hours. Oil of the same year, however, did not become siccative even by boiling with lime.

The oil dissolves very little of the small quantity of oxide of manganese, and the salt when removed may be repeatedly used in the preparation of drying oil. When prepared oil is mixed with an equal weight of crude oil, it requires nearly twice as long to dry; with twice the quantity, twenty hours longer; and with three times the quantity, another twelve hours; but the time necessary for the solidification of the coating gradually diminishes a little by long standing.—*Kunst- und Gewerbeblatt für Bayern*, 1856, p. 314.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 19, 1856. (The Lord Wrottesley, President, in the Chair.)

"Researches on Organo-metallic Bodies." Third Memoir.—On a New Series of Organic Acids containing Nitrogen. By Edward Frankland, Ph.D., F.R.S.

The author, in pursuing the line of research indicated in his former memoirs, has investigated the action of zincethyle and zincmethyle upon binoxide of nitrogen, and has succeeded in producing a new series of organic acids, by the substitution of oxygen in binoxide of nitrogen by methyle, ethyle, &c. Binoxide of nitrogen is slowly absorbed by zincethyle, and the sole product of the reaction is a body which is deposited in magnificent rhomboidal colourless crystals. This body has the composition expressed by the formula

$$N_2\,C_4\,H_5\,O_4\,Zn + C_4\,H_5\,Zn,$$

and consists of the zinc salt of a new acid, for which the author proposes the name *dinitroethylic acid,* united with zincethyle. The dinitroethylate of zinc and zincethyle is produced from binoxide of nitrogen and zincethyle according to the following equation,

$$\left.\begin{matrix}2(Zn\,C_4\,H_5)\\ 2NO_2\end{matrix}\right\} = N_2\,C_4\,H_5\,O_4\,Zn + C_4\,H_5\,Zn.$$

The crystals of dinitroethylate of zinc and zincethyle instantly become opake on exposure to the air, owing to the formation of an oxidized product. They are tolerably soluble in anhydrous ether without decomposition, but are instantly decomposed by anhydrous alcohol and by water. Exposed to the gradually increasing heat of an oil-bath, dinitroethylate of zinc and zincethyle fuses at 100° Cent., froths up, and begins slowly to evolve gas. At 180° the colour darkens, a small quantity of a highly alkaline liquid distils over, and a large amount of gas is evolved. The latter consists of carbonic acid, olefiant gas, hydride of ethyle, nitrogen and protoxide of nitrogen. When brought into contact with water, dinitroethylate of zinc and zincethyle is immediately decomposed with lively effervescence, due to the evolution of pure hydride of ethyle. An opalescent solution is formed, possessing a powerfully alkaline reaction and a peculiar bitter taste. The opalescent solution contains only basic dinitroethylate of zinc, and the reaction is expressed by the following equation :—

$$\left.\begin{array}{r}N_2C_4H_5O_4Zn+C_4H_5Zn\\ HO\end{array}\right\}=\left\{\begin{array}{l}C_4H_5, H\\ N_2C_4H_5O_4Zn+ZnO.\end{array}\right.$$

Carbonic acid decomposes this basic salt, precipitating carbonate of zinc, and leaving the neutral salt in solution.

Dinitroethylate of zinc and zincethyle is also decomposed by dry oxygen according to the following equation :—

$$\left.\begin{array}{r}N_2C_4H_5O_4Zn+C_4H_5Zn\\ O_2\end{array}\right\}=\left\{\begin{array}{l}N_2C_4H_5O_4Zn\\ ZnO\,C_4H_5O.\end{array}\right.$$

When the product of oxidation is treated with water, basic dinitroethylate of zinc is produced along with alcohol.

Neutral dinitroethylate of zinc crystallizes in minute colourless needles containing half an equivalent of water. It fuses at 100° Cent., and gradually becomes anhydrous. It is very soluble in water and in alcohol. Heated suddenly in air to about 300° Cent. it burns rapidly with a bluish green flame.

Dinitroethylic acid can only exist in dilute solution; it can be prepared, either by decomposing the zinc salt with dilute sulphuric acid and distilling *in vacuo*, or by decomposing the baryta salt by an exact equivalent of dilute sulphuric acid. The dilute acid thus prepared possesses a pungent odour, somewhat resembling that of the nitro-fatty acids, and an acid taste. It reddens litmus paper strongly, and gradually decomposes even at ordinary temperatures. Neutralized by the carbonates of the various bases, it yields the corresponding salts. The silver and magnesian salts thus prepared were analysed.

The salts of dinitroethylic acid are all soluble in water and in alcohol, and most of them crystallize with more or less difficulty. They are all violently acted upon by concentrated nitric acid, the dinitroethylic acid being entirely decomposed and a nitrate of the constituent base produced. Dilute nitric acid acts in the same manner, but more slowly. They all fuse at a temperature little above 100° Cent. The potash, soda, lime, and baryta salts deflagrate explosively, like loose gunpowder, at a temperature considerably below redness.

The following salts have been prepared and analysed:—

	Formulæ.
Dinitroethylate of silver	$N_2 C_4 H_5 O_4 Ag$
Double nitrate and dinitroethylate of silver	$N_2 C_4 H_5 O_4 Ag + NO_6 Ag$
Dinitroethylate of copper	$2(N_2 C_4 H_5 O_4 Cu) + HO$
Dinitroethylate of zinc (crystallized)	$2(N_2 C_4 H_5 O_4 Zn) + HO$
Dinitroethylate of zinc (anhydrous)	$N_2 C_4 H_5 O_4 Zn$
Dinitroethylate of zinc (basic)	$N_2 C_4 H_5 O_4 Zn + ZnO$
Dinitroethylate of zinc and zincethyle	$N_2 C_4 H_5 O_4 Zn + C_4 H_5 Zn$
Dinitroethylate of baryta	$N_2 C_4 H_5 O_4 Ba$
Dinitroethylate of lime	$N_2 C_4 H_5 O_4 Ca + 3HO$
Dinitroethylate of magnesia	$N_2 C_4 H_5 O_4 Mg$
Dinitroethylate of soda	$N_2 C_4 H_5 O_4 Na.$

Dinitromethylic acid.—When binoxide of nitrogen is absorbed by zincmethyle, dinitromethylic acid is produced, and forms a series of salts homologous with those of dinitroethylic acid. The formula of this acid is

$$N_2 C_2 H_3 O_4 H,$$

and the following salts have been examined:—

Dinitromethylate of zinc	$N_2 C_2 H_3 O_4 Zn + HO$
Dinitromethylate of soda	$N_2 C_2 H_3 O_4 Na + 2HO$
Dinitromethylate of zinc and zincmethyle	$N_2 C_2 H_3 O_4 Zn + C_2 H_3 Zn$?

It is difficult to arrive at any satisfactory conclusion relative to the rational constitution of this series of acids; they may be regarded as belonging to the type of nitrous acid, containing a double equivalent of nitrogen, and in which one atom of oxygen has been replaced by an alcohol radical, thus,

$$N_2 \left\{ \begin{array}{l} Cn\,Hn+1 \\ O \\ O \\ O \end{array} \right.$$

or they may be viewed as constructed upon the hyponitrous acid type, one equivalent of oxygen being replaced by an alcohol radical, and a second by binoxide of nitrogen, thus,

$$N \left\{ \begin{array}{l} Cn\,Hn+1 \\ NO_2 \\ O \end{array} \right.$$

Without attaching much value to either hypothesis, the author prefers the latter, and remarks in conclusion that there can be little doubt that many new series of organic acids may, by analogous processes, be produced from inorganic acids by the replacement of one or more atoms of oxygen by an alcohol radical; in fact his pupil, Mr. Hobson, is now engaged in the study of a new series containing sulphur, produced by the action of zincethyle and its homologues upon sulphurous acid. These acids are formed by the replacement of one equivalent of oxygen, in three equivalents of sulphurous acid, by an alcohol radical.

THE CHEMICAL GAZETTE.

No. CCCXXXIX.—December 1, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Production of Nitric Acid. *By* S. de Luca.

In a communication made to the Academy of Sciences at the commencement of this year, I have shown that by passing moist ozonized air over potassium and pure potash, nitrate of potash is obtained, which may be separated from the alkaline solutions by crystallization. After these results, which agree with those obtained by M. Schönbein by a different process, I wished to ascertain whether the oxygen disengaged from the leaves of plants by the action of the sun's light, or the air surrounding plants in vegetation, presented the properties of ozone.

I have not obtained concordant results in a great number of trials and experiments made with the detached and not detached leaves of different plants, or with entire plants, or in the vicinity of an abundant vegetation; litmus-paper is almost always discoloured, but iodized starch-paper only acquires a blue tint in certain cases. Thus with many plants of the *Cactus* family the iodized starch-paper is not coloured; it is sometimes coloured by the action of light in the presence of the green leaves of herbaceous plants, more rarely with those of the Rosaceæ, frequently in contact with or in the vicinity of turf, and very rarely in an inhabited locality.

Being unable to draw any certain conclusion from these results, which I had moreover announced to M. Malaguti at the beginning of last April, and the ozonometric paper being a very untrustworthy reagent, and capable of becoming coloured under the most different influences, I desired to make some comparative experiments between the air surrounding a considerable number of plants kept in a hot-house and the free air of the atmosphere in a locality at a distance from vegetation. For this purpose I set up an apparatus in a hot-house in the Botanic Garden of the Faculty of Medicine at the Luxembourg. An aspirator of 140 litres caused the air to pass slowly during the day, first through two glass tubes filled with carded cotton, then into sulphuric acid, afterwards over potassium, and finally into dilute solutions of pure potash. In fifteen days the potassium was changed into a syrupous solution of potash, which gradually became less concentrated. This apparatus was in action for about six months from the month of April in the present year.

The total volume of air which has traversed the apparatus may be approximatively calculated at more than 20,000 litres. The examination of the acid and alkaline liquids gave the following results:—The sulphuric acid contained ammonia, the presence of which was easily proved by means of potash and lime, by its characteristic odour, and the blue coloration of red litmus-paper. Of the three alkaline solutions, the first showed the reactions of nitric acid, and some little crystals of nitrate could even be obtained; in the other two, the reactions of the nitrates were ascertained, although crystals could not be isolated.

To check this experiment, I at the same time set up two pieces of apparatus in the court of the laboratory of the Collége de France. The first was composed of an aspirator of 150 to 160 litres, of two flasks, of which one contained solution of pure potash, and the other potassium in small globules; and the second of a similar aspirator, a flask containing solution of soda, and another flask with fragments of sodium. Each apparatus was furnished with a long glass tube, with plugs of carded cotton. The air traversed first the tube with the cotton, thus becoming freed from suspended matters; it then passed over potassium or sodium, and finally into the solution of potash or soda. These apparatuses have been in action almost continually during the day. The air employed in these two experiments may be valued approximatively at 17,000 litres for one apparatus, and at 19,000 litres for the other. For one month only in each apparatus I interposed a tube with five bulbs, containing dilute sulphuric acid, between the cotton-tube and the flasks with potassium and sodium. The following are the results of these two experiments:—

I have ascertained the presence of ammonia in the sulphuric acid of each apparatus. This ammonia was evidently derived from the atmosphere. I was unable to ascertain the presence of the least quantity of nitric acid in the solutions of potash and soda, and in the liquids derived from the potassium and sodium.

These facts show that alkaline solutions do not produce nitrates during the day with a current of air containing ammonia, when this current is produced far from the vegetation of plants; and that, on the contrary, the air of a hot-house in which a great number of plants of all kinds are vegetating produces nitrates with alkaline solutions, even after traversing sulphuric acid, and thus becoming freed from ammonia. Is this because the plants act like porous bodies upon the elements of nitric acid contained in the atmosphere? Direct experiments, made far from vegetation with porous bodies derived from the mineral kingdom, prove the contrary, for they do not furnish nitrates.

The beautiful experiments of Prof. Andrews confirm the opinion that ozone, far from being a peroxide of hydrogen, is nothing but modified oxygen, capable of being analysed with the greatest exactitude. On the other hand, the phænomena of oxidation which ozone can produce are not rare, and we know what advantage may be derived, for chemical analysis, from ozonized oil of turpentine, from the ozone produced by the combustion of æther in contact with platinum, &c. We know also that urea is formed in the blood of the animal œconomy; and M. Béchamp has shown that this body is produced artificially by the oxidation of albuminoid substances by means of the permanganate of potash.

It is not improbable that the oxygen of the air introduced into the œconomy by the phænomenon of respiration, and retained condensed or modified by the globules of the blood in presence of an alkaline material, exists there, in part, in the state of ozone, like the oxygen dissolved in turpentine, and consequently in a condition to produce the same phænomena of oxidation. These views find support in some experiments made with permanganate of potash, the oxygen evolved from which by sulphuric acid presents the properties of ozone, even at a low temperature; and in the recent researches of M. Schönbein with regard to the property possessed by the juice of some mushrooms, of transforming oxygen into ozone.

If now we were to bring together these facts, in order to explain the results which I have just obtained, we should be tempted to admit that the oxygen which is disengaged from the leaves of plants by the action of light contains ozone, or that the air surrounding the plants has become partially ozonized, and that this ozone, although in small quantity, produces the oxidation of the nitrogen of the air to form nitric acid, in the same way that ozone artificially prepared produces nitrates with air and alkalies. The question of the absorption of nitrogen by plants would consequently be reduced to the pure and simple absorption of a nitrogenous compound, such as the nitrate or carbonate of ammonia, this carbonate being capable of formation in the atmosphere, and the nitrate of originating under the influence of vegetation.—*Comptes Rendus*, Nov. 3, 1856, p. 865.

On some new Platino-cyanides. By P. P. Weselsky.

The author has studied the products of the action of nitric acid upon the double protocyanides of platinum.

1. He first exposes them, under an exsiccator, to the fumes of nitric acid;
2. Treats them, when crystallized and powdered, with nitric acid of spec. grav. 1·3 at the ordinary temperature; and
3. Adds the nitric acid to the saturated solution, and allows the fluid to evaporate spontaneously.

The platino-cyanide of barium serves as the original substance; this the author prepared in a new way. A mixture of protochloride of platinum and carbonate of baryta is diffused in water. Hydrocyanic acid is passed into it, and thus chloride of barium and platino-cyanide of barium are obtained. This salt, which according to the investigations of Quadrat and Schafarik* is best purified by recrystallization, on account of its difficult solubility, and best produced, on account of its base, by the mutual decomposition of the salts of other bases, serves also in these experiments for the production of the different platino-cyanides of the formula of Gmelin's salts, which then, when treated with nitric acid, furnish new salts.

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* Chem. Gaz., vol. vi. p. 109, and vol. xiii. p. 441.

The Potassium Compound, $K^2 Pt^2 Cy^5 + 6HO$, was obtained by the author with all the properties described by Knop (it is his sesquicyanide of potassium and platinum, $Pt^2 Cy^3 + 2KCy + 5HO$), but with 6 atoms of water instead of 5, which Knop found. (In Knop's analyses it is stated, that the amount of water may easily turn out variously by the efflorescence of the salt.)

The Ammonium Compound, $Am^2 Pt^2 Cy^5$ (Knop's sesquicyanide of platinum and ammonium, $Pt^2 Cy^3 + 2AmCy$).

The Lithium Compound, $Li^2 Pt^2 Cy^5 + 6HO$, a salt resembling the preceding (also a salt with a coppery metallic lustre), but much more readily soluble in water.

The Magnesium Compound, $Mg^2 Pt^2 Cy^5 + 14HO$, as a blackish-violet, satin-like mass of microscopic needles.

Yellow Platino-cyanide of Magnesium, $Mg, Pt, Cy^2 + 6HO$.—Schafarik has repeatedly stated, that under certain circumstances the solution of platino-cyanide of magnesium does not furnish the beautiful metallic green crystals, but instead of these yellow crystals.

The author has found that this yellow salt is obtained when the saturated aqueous solution of the ordinary platino-cyanide is exposed to a temperature of 113° to 122° F. at the utmost, or when the alcoholic solution of the ordinary salt is left standing under the exsiccator. Laminæ of a citron-yellow colour, several lines in length and a line in breadth, are then obtained. This salt is best obtained with 6 atoms of water, when the hot saturated solution is left in a beaker for a long time in an air-bath of the temperature above mentioned.

Red Platino-cyanide of Hydrogen with 5 equivalents of Water, $PtH, Cy^2 + 5HO$.—When platino-cyanide of barium or potassium is decomposed by concentrated instead of dilute sulphuric acid, and the cyanide separated by æther and alcohol from the sulphate of potash or baryta, the evaporation of the ætherial alcoholic solution under the exsiccator furnishes a splendid red compound, which has already been observed by Quadrat, when he treated platino-cyanide of potassium with sulphuric acid. The compound is obtained in beautiful red determinable crystals. These are 7 to 8 lines long, half a line thick, splendid vermilion-red with a blue surface-lustre upon the prismatic surfaces, which appear of a beautiful vermilion when looked at perpendicularly to the axis. In the air they soon acquire the appearance of platino-cyanic acid. They are readily soluble in water, alcohol, or a mixture of alcohol and æther; towards carbonic acid the body acts as a strong acid, and when moistened with muriate of ammonia forms platino-cyanide of ammonium.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xx. p. 282.

On the Behaviour of Iodide of Mercury to Ammonia, and a new Reaction for Ammonia. By JULIUS NESSLER.

When a current of dry ammoniacal gas is passed over iodide of mercury, the latter becomes white, and takes up, according to Rammelsberg, ½ an equiv., and according to H. Rose, after a longer exposure, 1 equiv. of ammonia. In this way the two compounds $NH^3, 2HgI$ and NH^3, HgI are produced. Both lose all their ammonia even below 32° F., and pass again into iodide of mercury.

In liquid ammonia, according to Caillot and Carriol, iodide of mercury first becomes white, a portion is dissolved, and another becomes brown; when the fluid is evaporated, white crystals are produced, and the mother-liquor contains iodide of mercury and iodide of ammonium. Böttger also remarks that iodide of mercury gives with liquid ammonia a brown powder and a yellow fluid, from the latter of which white flakes are deposited. According to Wittstein, iodide of mercury under liquid ammonia becomes white, and when heated brownish-red.

Rammelsberg investigated the brown compound produced by the action of liquid ammonia upon iodide of mercury when heated, and considered it as an amide compound of the formula $HgI + 2HgO + HgNH^2$. Rammelsberg also prepared a compound, $NH^3, 2HgI$, in the humid way; it is always produced, according to his statements, by the action of liquid ammonia upon iodide of mercury, or solution of iodide of mercury and iodide of potassium.

By slowly pouring concentrated liquid ammonia into a solution of iodide of mercury and iodide of potassium, the author obtained two bodies differing in colour and crystalline form, and found that this solution, when a free fixed alkali is present, is a sensitive reagent for ammonia. This induced him to examine the behaviour of solution of iodide of mercury and iodide of potassium, and of iodide of mercury alone towards liquid ammonia of various degrees of concentration, with and without the action of free fixed alkalies.

I. *Behaviour of Solution of Iodide of Mercury and Iodide of Potassium towards Ammonia.*—In a dilute solution a little ammonia produces no precipitate. In a concentrated solution, pale, yellowish, acicular crystals are soon produced, and with a large quantity of concentrated ammonia these crystals are white.

For the preparation of these compounds, equal equivalents of iodide of mercury and iodide of potassium were dissolved in a little water. The solution (1 cub. centim. of which contained 0·20 HgI), mixed with ½ an equiv. of liquid ammonia (1 cub. centim. containing 0·05 NH^3), gave few crystals after long standing. These increased by the addition of further portions of ammonia, but it was only when the fluid had received 4 equivs. of ammonia to 1 equiv. of iodide of mercury that other crystals appeared to be produced. Most of the fluid was poured away, and a portion of it was mixed with very concentrated liquid ammonia, whilst ammoniacal gas was passed through another; both fluids furnished long white needles, whilst the crystals first obtained were yellowish and possessed a different crystalline form, which however could not be determined, as the crystals, when taken out of the fluid, were immediately decomposed into iodide of mercury and ammonia; they appeared to consist of quadratic prisms.

For examination, the yellowish crystals were dried as quickly as possible in a cold room (in winter) between blotting-paper, and put into a dry weighed tube, which was drawn out a little at one end and furnished with a stopper of asbestos; a second weighing gave the weight of the crystals. The tube was then filled with cotton-wool dried at 212° F., and again weighed, when its narrower end was united with two consecutive vessels containing concentrated sulphuric acid, and its wider end with a W-tube, which contained sulphuric acid of known strength. Air was then drawn through it by an aspirator, in such a way that it must pass first through the concentrated sulphuric acid, then through the tube with the crystals, and finally through the sulphuric acid in the W-tube. In a few hours the crystals became red, when they were heated at first gently, but afterwards rather more strongly, until the weight remained the same at two weighings. The decomposition was not assisted by heat at first, because by this means the compound $HgI, 2HgO, Hg, NH^2$, described by Rammelsberg, might readily have been produced, although in small quantity.

After the deduction of water, the analysis led to the formula $NH^3, 2HgI$. It gave,—

	I.	II.		
HgI	96·12	96·07	2	96·38
NH^3	3·88	3·93	1	3·62

The analysis of the white crystals gave,—

	I.	II.		
HgI	96·92	92·84	1	93·00
NH^3	7·04	7·16	1	7·00

II. *Behaviour of Iodide of Mercury towards concentrated Ammonia.*—By pouring liquid ammonia over iodide of mercury, Rammelsberg obtained the compound $NH^3, 2HgI$; and by the employment of very concentrated ammonia, the compound NH^3, HgI may also be produced in more or less time. With liquid ammonia, saturated in the cold, iodide of mercury was converted into this compound in half an hour; with less concentrated ammonia the operation takes longer, and a slight addition of iodide of potassium facilitates the action.

To ascertain how much ammonia was taken up by a determinate quantity of iodide of mercury, 12 grms. of the latter were triturated with 5 cub. centims. of solution of iodide of potassium, put into a vessel capable of being well closed, and treated with 70 cub. centims. of a liquid ammonia which contained 0·064 of ammonia in the cubic centimetre. The action was assisted by frequent shaking; and the next day, as the compound had become white, 5 cub. centims. of the clear supernatant fluid were diluted with water, and neutralized with a solution of oxalic acid containing 0·01 of C^2O^3, HO in the cubic centimetre, for which purpose 65·7 cub. centims. were required. 75 cub. centims. would have required 985·5 cub. centims. of solution, or 9·855 grms. of oxalic acid, representing 3·72 of ammonia. The 70 cub. centims. employed contained 70 × 0·064 = 4·48 grms. The 12 grms. of iodide of mercury consequently took up 0·76 (4·48–3·72), or 6·33 per cent. of ammonia. The fluid was then poured off, and replaced by more concentrated ammonia. The analysis of the compound gave,—

HgI	91·98	1	93·00
NH^3	8·02	1	7·00

The analyses enable no conclusion to be drawn as to whether the water contained in the compound is to be regarded as chemically combined, as water of crystallization, or as adherent. H. Rose prepared the compound NH^3, HgI in an anhydrous state in the dry way; the white crystals may therefore be regarded as identical with that compound, and anhydrous. Rammelsberg found so little water in the crystals of the composition NH^3, 2HgI described by him, that they are to be regarded as anhydrous. From the ætherial solution, anhydrous crystals of the composition NH^3, HgI may be obtained, which however does not prove that those obtained from an aqueous solution contain no water of crystallization. The crystalline form indeed is similar, but the identity or dissimilarity of the two compounds could not be ascertained, as they are decomposed in the air.

To prepare a compound free from adherent water, the white body obtained by the action of liquid ammonia upon iodide of mercury was dissolved in æther, and a greater part of this solution was evaporated at a gentle heat in a current of ammoniacal gas. In the fluid remaining, very long lance-shaped crystals were formed, but only when the vessel containing it had been left uncovered for a long time. The compound is more soluble in æther containing ammonia. The crystals have the following composition:—

	Found.	Calculated.
HgI	92·98	93·00
NH^3	7·02	7·00

corresponding with the formula NH^3, HgI.

III. ***Behaviour of Iodide of Mercury with dilute Liquid Ammonia.***—If water be poured over iodide of mercury (in the experiment, 10 grms. HgI and 200 cub. centims. HO were employed), and ammonia be then added in small portions with frequent shaking, the fluid soon contains iodides of ammonium and mercury, and a brown body remains undissolved, which becomes brownish-red on exposure to the air, and is again rendered brown by ammonia, but is no longer converted into a white compound by concentrated liquid ammonia, as is the case with iodide of mercury.

The brown body thus obtained may perhaps be regarded as a mixture of $NHg^4I + 2HO$(HgI, 2HgO, Hg, NH^2 according to Rammelsberg), NH^3, 2HgI and HgI, in which one or the other constituent predominates according to the quantity of water and liquid ammonia present, and the duration of the action. The greater or less quantity of $NH^3,2HgI$ is the cause of the body being more or less red when exposed to the air. After frequent digestion with æther, a brown compound remains, which agrees in all its properties with the compound NHg^4I+2HO.

On the Decomposition of the Compound NH^3,HgI.—If a large quantity of water be poured over the compound NH^3,HgI, it extracts all the ammonia from it, and pure iodide of mercury remains. If, on the contrary, the water be added in small quantities, or if it contains ammonia, the compound first becomes yellow, and when left to stand for a long time, passes through numerous intermediate shades to brown. The yellow body first obtained is also decomposed by much water or by drying, into ammonia and pure iodide of mercury; but the more it has become brown, the more does the red colour of the body remaining after drying or washing pass to brown, until at last, with the right proportion of water to the compound NH^3,HgI (which however varies with the temperature), and sufficiently long action, a brown body is produced, which undergoes no change in drying. It consists probably of $NHg^4,2HO$, with which more or less iodide of mercury is mixed, according as pure water or water containing ammonia has been employed.

The compound NH^3,HgI is decomposed in the air into ammonia, which is evolved, and a residue of iodide of mercury; this decomposition takes place more rapidly in an attenuated atmosphere. In closed vessels the compound loses ammonia, until the pressure produced by this + the affinity of the ammonia for the iodide of mercury, overcomes its elasticity. The compound becomes more or less yellow according to the size of the vessels.

If the compound NH^3,HgI be sealed up in a tube with iodide of mercury and gently heated, the whole contents of the tube soon become uniformly yellow.

The decomposition by a large quantity of water is caused by the greater affinity of ammonia for water than for iodide of mercury. In proportion as the water takes up ammonia, its affinity for that body becomes less; a period must therefore arrive with sufficiently small quantities of water, when the tendency of the latter to take up ammonia no longer outweighs the affinity of ammonia for iodide of mercury. This equilibrium of the affinities soon occurs when the water only contains a small quantity of ammonia; but the affinity of water to iodide of ammonium is little, if at all prejudiced by this; it causes, or essentially aids in the formation of this iodide. Iodide of ammonium and NHg^4I+2HO are produced slowly, and only in the presence of a good deal of water at ordinary temperatures, but more rapidly and with less water with the aid of heat:—

$$4NH^3HgI+Aq=NHg^4I+Aq+3NH^4I.$$

If a little alcohol be poured over the compound NH^3HgI, a portion of it is dissolved, and another portion becomes yellow. This yellow body is converted into a brown one by much alcohol. The fluid contains iodide of ammonium, iodide of mercury, and NH^3,HgI, the latter of which is thrown down as a white powder on the addition of water, but soon becomes red by loss of ammonia.

Alcohol therefore behaves towards this compound (except the solubility) like water containing a certain quantity of ammonia; it assists in the formation of iodide of ammonium, without however possessing sufficient affinity for ammonia to decompose the compound $NH^3 HgI$ or $NH^3 2HgI$ into ammonia and iodide of mercury. Æther dissolves a portion of the compound, and another portion becomes yellow. The brown body is not formed.

IV. ***Behaviour of Solution of Iodide of Potassium and Iodide of Mercury towards Ammonia in the Presence of Free Potash or Soda.*** —If free potash and ammonia be added to a solution of iodide of potassium and mercury, a yellowish-brown precipitate is formed, which is paler with a small, and darker with a larger quantity of potash. It soon becomes kermes-brown, especially in the presence of a great excess of potash, and in its properties resembles the compound obtained by Rammelsberg by heating iodide of mercury with liquid ammonia. From its per-centage composition it may be regarded as $HgH^2 N+2HgO+HgI$ or $NHg^4 I+2HO$.

The action of potash and ammonia upon the iodides of mercury and potash would therefore be as follows:—

$$4(HgI+KI)+3KO+NH^3=[NHg^4 I+2HO]+7KI+HO.$$

For the investigation of this reaction, 10·25 grms. of iodide of mercury were dissolved with 1 equiv. (7·67 grms.) of iodide of potassium in 205 cub. centims. of water, and to 4 equivs. HgI 1 equiv. ammonia and 3 equivs. of potash were added by means of normal solutions. The clear fluid was poured away from the precipitate produced, which became brown after long standing; the precipitate was washed by decantation, and dried at 212° F., when it weighed 1·76 grm.

The combined fluids gave another precipitate on the addition of ammonia and potash; this, when removed from the fluid after long standing, washed and dried, weighed 2·26 grms.

The fluid with this last precipitate amounted to 475 cub. centims. The bases hitherto added (ammonia and potash) would have been saturated by 7·2 of anhydrous sulphuric acid. 10 cub. centims. of the 475 required for neutralization 0·126 grm. sulphuric acid (12·6 cub. centims. of a sulphuric acid containing 0·01 SO^3 in the cubic centimetre); 475 cub. centims. would therefore have required 5·98 grms. SO^3, or 1·22 grm. less than the bases employed.

According to the formula—

$$4(HgI, KI)+3KO+NH^3=\left[\begin{matrix}NHg^4 I+2HO\\ Aeq=559\end{matrix}\right]+7KI+HO,$$

to form 559 grms. of the compound, 3 equivs. of potash and 1 equiv. of ammonia are neutralized, which correspond with 4 equivs. $SO^3=160$ grms. Up to this time $1·76+2·26=4·02$ of the brown compound were obtained. $559:160=4·02:1·15$; hence for the neutralization of these 475 cub. centims., 1·15 less acid must be necessary than would have been required by the bases employed; the experiment gave 1·22.

260 cub. centims. of the 475 were mixed with a concentrated solution of potash as long as any precipitate was produced. After long standing, the clear decanted fluid acidulated with muriatic acid gave no further turbidity with sulphuric acid; it was therefore free from mercury. The brown precipitate obtained was well washed and dried; it weighed 1·18 grm. 260 cub. centims. gave 1·18; 475 cub. centims. would have given 2·15.

Of 10·25 grms. of iodide of mercury, therefore, there would have been obtained 1·76+2·26+2·15=6·17 grms. By the calculation—

908	:	559	=	10·25	:	6·30
4 equivs. HgI	:	NHg^4+2HO	=	employed HgI.		

6·30 grms. should have been obtained.

The analysis of the brown body gave,—

	Found. I.	Found. II.	Calculated.
Mercury	71·32	71·92	71·69
Nitrogen	2·34	2·47	2·51
Iodine	..	23·46	22·58
Hydrogen	..	..	0·36
Oxygen	..	..	2·86

corresponding with the formula $HgI, 2HgO, HgNH^2$ or $NHg^4 I, 2HO$.

Constitution of these Compounds.—Four views prevail with regard to the constitution of the bodies produced by the action of ammonia and ammoniacal salts upon compounds of mercury.

The first considers them as compounds of ammonia or anhydrous ammoniacal salts with compounds of mercury,—

e. g. NH^3+2HgI and NH^3, NO^5+3HgO.

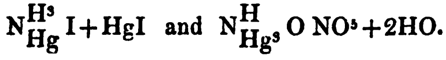
In the second they are regarded, after Kane, as compounds of hydrargyramide with other mercurial or amide compounds,—

e. g. $Hg, H^2 N+3HgI+H^3 N, HI$ and $Hg, H^2 N+2HgO, NO^5$.

The third, that of Hirzel, supposes the presence of nitruret of mercury in the compounds,—

e. g. $Hg^3 N+HgI+3(NH^3, HI+HgI)$ and
$Hg^3 N+3HgO, NO^5+NH^3, HO, NO^5$.

The fourth, or Gerhardt's, considers them as ammonium compounds in which one or more atoms of hydrogen in the molecule of ammonium are replaced by mercury,—

e. g. 
$N\overset{H^3}{\underset{Hg}{}} I+HgI$ and $N\overset{H}{\underset{Hg^3}{}} O\,NO^5+2HO$.

Weltzien has recently supported this view, and given many of the compounds in question their corresponding formulæ.

The first of these views cannot be adopted for all the compounds, but then it is improbable that an anhydrous ammoniacal compound of an oxyacid is produced in the presence of water, and lastly ammonia cannot generally be expelled from these compounds by potash.

The formulæ, according to the two following views, are rather complicated, and besides many productions and decompositions are explained by them with difficulty. Thus according to the formulæ $Hg^3N+HgI+3(Hg^3N, HI+HgI)$ or $HgH^2N, 3HgI+H^3N, HI$, it is difficult to see how the compound in question is decomposed into iodide of mercury and ammonia at a temperature below 32° F., or by the addition of a large quantity of water.

The formulæ according to the fourth view are more simple, and the mode of production and decomposition of the compounds are explained thereby without difficulty.

The modes of preparation of these compounds are shortly as follows:—

1. Dry ammoniacal gas is passed over peroxide of mercury, or a haloid compound corresponding with this.

At a high temperature, with peroxide of mercury, nitruret of mercury and water are produced, $3HgO+NH^3=NHg^3+3HO$; with peroxide of mercury and iodide of mercury we get water and iodide of tetramercammonium,—

$$3HgO, HgI+NH^3=[NHg^4I+2Aq]+HO.$$

At a lower temperature ammonia combines with the haloid compounds as with hydracids, and monomercammonium compounds are produced, $NH^3+HgI=N^{H^3}_{Hg}I$. With an excess of the haloid salt of mercury, acid compounds are produced, $N^{H^3}_{Hg}I+HgI$.

2. Peroxide of mercury is boiled with liquid ammonia; we get

$N^{H}_{Hg^3}O, 4HO$, according to Kane's analysis, and

$NHg^4O, 3HO$, according to that of Millon,

$NH^3+4HgO=NHg^4O+3HO$.

3. Solutions of persalts of mercury or of the corresponding haloid compounds are mixed with liquid ammonia. According to the concentration of the fluids, the temperature, and the degree of solubility of the salts, various compounds are produced. At a high temperature, and with sufficiently dilute solutions, tetramercammonium compounds are generally produced.

Nitrate of mercury in solution with ammonia (not in excess) gives nitrate of the oxide of trimercammonium and NH^4O, NO^5,—

$$3(HgO, NO^5)+2NH^3=N^{H^2}_{Hg^2}O, NO^5+2(NH^4, NO\ O^5).$$

But if the solution already contain NH^4O, NO^5, less of this is formed, and we obtain nitrate of the oxide of bimercammonium,—

$$2(HgO, NO^5)+2NH^3=N^{H^2}_{Hg^2}O, NO^5+NH^4O, NO^5.$$

If however the affinity of the water to the NH^4O, NO^5 be increased by heat, more of the latter is produced, and nitrate of the oxide of tetramercammonium is formed,—

$$4(HgO, NO^5)+4NH^3=NHg^4O, NO^5+4(NH^4O, NO^5).$$

If a solution of HgO, NO^5 be mixed with a great excess of ammonia, $\begin{matrix}NHg^4O\\2HgO\end{matrix}+NO^5$ is produced.

Solution of bichloride of mercury, mixed with liquid ammonia, furnished at ordinary temperatures $N\begin{matrix}H^2\\Hg^2\end{matrix}Cl$ and NH^4Cl,— $2HgCl+2NH^3=N\begin{matrix}H^2\\Hg^2\end{matrix}Cl+NH^4Cl$. At a higher temperature, and with sufficient dilution, $NHg^4Cl+2HO$ is produced,—

$$4HgCl+4NH^3+2HO=NHg^4Cl, 2HO+3NH^4Cl.$$

If the solution be previously mixed with NH^4Cl, $N\begin{matrix}H^3\\Hg\end{matrix}Cl$ is produced, and no chloride of ammonium is formed.

4. Peroxide of mercury, its oxysalts, and the corresponding haloid compounds are treated with salts of ammonia. According to the concentration of the fluids and the temperature at which the decomposition takes place, various compounds may be produced in this case also.

If peroxide of mercury be put into a cold solution of acetate of ammonia, acetate of the oxide of monomercammonium is produced, when boiled acetate of the oxide of tetramercammonium is formed.

5. Ammonium compounds, in which 1, 2, or 3 atoms H are already replaced by Hg, are boiled with water or alkalies. Tetramercammonium compounds are produced; when water is employed, ammonium compounds are formed, and with alkalies ammonia is set free.

6. Compounds of protoxide of mercury, or the corresponding haloid compounds, are treated with ammonia.

The addition of a small quantity of ammonia to a solution of protonitrate of mercury produces a black precipitate, which may be regarded as basic protonitrate of mercury, according to Mitscherlich with 3, according to Kane with 2 equivs. of protoxide, of which the one, instead of 2Hg, contains 1Hg and $1N\begin{matrix}H^3\\Hg\end{matrix}$; it is represented therefore by the formula $N\begin{matrix}Hg\\(H^3Hg)O\\2Hg^2O\end{matrix}, NO^5$. If ammoniacal gas be passed over precipitated protochloride of mercury, the latter takes up 1 equiv. of ammonia, and becomes converted into a black powder, which may be regarded as $N\begin{matrix}Hg\\(H^3, Hg)\end{matrix}Cl$.

By treating protochloride of mercury with liquid ammonia, a black compound is also produced; this may be regarded as subchloride, consisting of 2 equivs. of mercury, 1 equiv. of bimercammonium, and 1 equiv. of chlorine, $N\begin{matrix}(Hg^2H^2)\\Hg^2\end{matrix}Cl$, and probably corresponds with the subchloride of mercury obtained by A. Vogel.

By the treatment of peroxide of mercury with solutions of various amides, Dessaignes obtained compounds which he considered as composed of peroxide of mercury and the amides in question. They may perhaps better be regarded as amides, in which 1 H is displaced by 1 Hg, and the more because with some of them water is separated on entering into combination with the peroxide of mercury. Thus, for example, the compound obtained with butyramide would be

$$C^8H^7O^2, N\begin{matrix}H\\Hg\end{matrix}.$$

[To be continued.]

On the Presence of Fluorine in the Blood. By J. Nicklès.

In consequence of considerations which I shall shortly submit to the Academy, I have been led to verify the assertion, so often disputed, of the presence of *fluorine in the bones.* My experiments have been affirmative; I have sought for fluorine in the blood, the only way by which it could have arrived at the bony tissue. I have found it in considerable proportions, not only in the human blood, but also in that of several Mammalia (the Pig, Sheep, Ox, Dog) and Birds (Turkey, Duck, Goose, Fowl).

Such concordant results appear to give an importance to fluorine in medicine and physiology, which it has not hitherto possessed; they evidently invalidate the opinion of Berzelius, according to which the presence of fluorine in the bones is purely accidental, and in any case unnecessary.

If other proofs were required of the necessity of revising the judgement of this illustrious chemist, we should find them in the following facts:—There is fluorine in the bile, in the albumen of the egg, in gelatine, in the saliva, in the urine, in the hair, and in the hairs of animals (Ox, Cow and Calf); in one word, the animal organism is penetrated by fluorine; we may expect to find it in all the liquids which impregnate it.—*Comptes Rendus,* Nov. 3, 1856, p. 855.

Note on the Alloys of Aluminium. By C. *and* A. Tissier.

The authors state, that aluminium, like zinc, is injured in its properties by an admixture of foreign metals, which in giving it hardness deprive it of a great part of its malleability. A twentieth of iron or copper render it almost impossible to work aluminium; a tenth part of copper renders it as brittle as glass, and gives it the property of blackening in the air; silver and gold harden it, but to a much less extent.

An alloy of 5 parts of silver to 100 of aluminium can be worked like the latter metal in a state of purity, and has the advantage of being harder and capable of a finer polish. A tenth part of gold deprives aluminium of none of its malleability; and the alloy thus formed, although harder than aluminium, is much less so than that with 5 per cent. of silver. A thousandth part of bismuth hardens aluminium to such a degree that it cracks under the hammer, notwithstanding repeated annealing.

The addition of aluminium to other metals is often attended with good results, if the quantity of aluminium be not too great. A twentieth part of aluminium gives copper the brilliancy and fine colour of gold, and at the same time sufficient hardness to scratch the alloy of gold employed in coin, without any injury to its malleability.

A tenth part of aluminium with copper produces an alloy of a pale gold colour, possessing at once great hardness and considerable malleability, and capable of taking a brilliancy equal to that of polished steel.

5 parts of aluminium with 100 parts of pure silver give an alloy almost as hard as the silver used in money, which contains a tenth of copper, so that sufficient hardness may be given to silver without introducing a poisonous or alterable metal. Here again aluminium does not alter the qualities of silver.—*Comptes Rendus*, Nov. 3, 1856, p. 885.

ANALYTICAL CHEMISTRY.

On some new Reactions of Oxide of Chrome. By G. Chancel.

In some Treatises on Chemistry, it is recommended, as a means of separating at once chromium and zinc from the other metals contained in a solution, the treating of the latter with an excess of caustic potash, so as only to dissolve the oxides of chromium and zinc (as well as alumina). This reaction can never have been executed in practice, for, according to my experiments, chromium and zinc cannot coexist in a solution of potash, as they mutually precipitate each other. In fact, when we mix together two solutions, one of oxide of chromium and the other of oxide of zinc in potash, the solution which is employed in excess precipitates the other completely. In this way a green precipitate is obtained, which when washed and dried contains—

$$Cr^2 O^3, ZnO,$$

and consequently presents a composition similar to that of chromic iron, magnetic oxide of iron, and the compounds of oxide of chromium with different bases, recently obtained by M. Pelouze.

The same reaction is observed between oxide of chromium and oxide of lead, both dissolved in potash; a green precipitate is also obtained, in which I have found the proportions—

$$Cr^2 O^3, PbO.$$

I have observed another fact which may be employed in the analysis of the chromic compounds. Whenever we have oxide of chromium in solution in potash, or simply mixed with this alkali, it is sufficient to add puce-coloured peroxide of lead to the solution or mixture, and heat it gently to dissolve the whole of the chromium in the state of chromate of lead. In this way a yellow liquid is obtained, which, when freed from the excess of peroxide of lead by filtration, deposits the chromate of lead on supersaturation with acetic acid.

The preceding reaction furnishes a simple means of converting oxide of chrome into chromic acid. This transformation in the humid way is much more rapid and convenient in its execution than the transformation in the dry way (by means of nitrate of potash), generally employed in laboratories.—*Comptes Rendus*, Nov. 10, 1856, p. 927.

On the Quantitative Determination of Oxide of Lead.
By A. Vogel, Jun.

The author has found that sulphate of lead, precipitated from solutions containing nitric acid, is never free from that acid. (This is the case also with baryta-salts, but in these it is ascertained that nitrate of baryta is retained.) The author supposes that free nitric acid is retained. In determinations of lead, therefore, the precipitate thrown down by sulphuric acid is to be dried at 212° F., and a portion of it calcined; in this way the nitric acid will be expelled, the loss of the portion employed is determined, and from this the value for the whole precipitate dried at 212° F. is calculated.

When the lead is thrown down by sulphuretted hydrogen from lead compounds containing zinc acidulated with sulphuric acid, the sulphuret of lead precipitated always contains sulphuret of zinc.

Lead does not form an alloy with zinc; if the two metals be fused together, the uppermost layer is zinc free from lead, the lower one lead containing 1·5, or perhaps rather more zinc. An addition of tin, namely $Zn : Pb : Sn = 1 : 1 : 1$, produces an alloy.—Buchner's *neues Repert.*, v. p. 289.

Note on the Quantitative Determination of the Sulphur in Mineral Waters. By J. Maxwell Lyte.

The process of Dupasquier usually employed for this purpose has been shown to be inexact. The solution of iodine in alcohol is gradually decomposed, with formation of hydriodic acid. This inconvenience has been remedied by dissolving the iodine in a solution of an iodide. But in certain springs, probably more than is supposed, there exist hyposulphites, the presence of which renders Dupasquier's process inexact, as iodine is changed into hydriodic acid by hyposulphurous acid, as well as by sulphuretted hydrogen.

The author proposes to precipitate the sulphur as sulphuret of silver by means of the double hyposulphite of silver and soda dissolved in an excess of hyposulphite of soda. This reagent is prepared by dissolving chloride of silver in a solution of hyposulphite of soda; it may be kept for a long time, especially with the addition of 1 or 2 drops of ammonia. The employment of nitrate of silver, dissolved in an excess of ammonia, has already been proposed; but in this case the iodides which may be present will be precipitated, and if the excess of ammonia be not very great, or if the water contains carbonic acid, the chlorides and bromides will also be precipitated, as will also be the case with organic matters, especially with the contact of light or heat if the spring be hot.—*Comptes Rendus*, Oct. 20, 1856, p. 765.

PROCEEDINGS OF SOCIETIES.

Royal Society.

April 17, 1856.—The Lord Wrottesley, President, in the Chair.

The following communication was read:—

"On the Condition of the Oxygen absorbed into the Blood during Respiration." By George Harley, M.D.

The author commences by explaining, that his researches were instituted with the view of ascertaining whether the doctrine maintained by Magnus in regard to the gases interchanged in the lungs during respiration were correct—namely, that the gases in question enter into *no* chemical combination with the constituents of the blood, either in passing to or from the tissues and organs of the body, but form merely a physical mixture with the circulating liquid. The principal object of the inquiry was to determine the following points:—

1. Has blood the property of chemically combining with the respired oxygen?
2. Which of the constituents of the blood enter into combination with oxygen?
3. Do these constituents, by combining with oxygen, simply become oxidized, or do they also yield carbonic acid gas?
4. What are the agents which control these changes?

After describing the method of investigation, and the apparatus employed, the author proceeds to relate a few of the analyses which he considered as the most conclusive. Instead of confirming the view of Magnus, that gases enter into no chemical combination with blood, his results led him to conclusions of an opposite character, which serve to confirm the more generally received doctrine.

In one set of experiments a certain quantity of fresh ox-blood was first shaken with renewed portions of air until it had become thoroughly saturated with oxygen, then introduced into a graduated glass vessel with 100 per cent. of ordinary air, corked carefully up, and kept during twenty-four hours in a room of moderate temperature. In order to favour the mutual action of the air and blood, the vessel was frequently agitated. At the expiration of twenty-four hours the gas was analysed by Bunsen's method. In an example cited the following was found to be its composition:—

Oxygen	10·42	total oxygen = 15·47
Carbonic acid	5·05	
Nitrogen	84·53	
	100·00	

On comparing this with the composition of the common air (oxygen 20·96; carbonic acid 00·002; nitrogen 79·038) which had been introduced into the vessel, it is seen that 10·54 per cent. of oxygen has disappeared, while 5·05 per cent. of carbonic acid now exists, where only a trace of its presence could before be detected.

Similar results were obtained with defibrinated blood. In a case where defibrinated arterial blood from a calf, after complete saturation with oxygen, was kept in contact with an equal volume of air during twenty-four hours, and treated exactly as in the previous example, the gas on analysis yielded in 100 parts,—

Oxygen	11·33	total oxygen = 17·29
Carbonic acid	5·96	
Nitrogen	82·71	
	100·00	

showing in this case also that the air which had been imprisoned during twenty-four hours along with blood, no longer possessed its original composition, but that some of its constituents had been materially increased, while others had diminished in a manner no less marked.

It would appear from these examples that the blood had probably become oxidized in two ways; first, by giving off a quantity of carbon, and secondly by directly combining with oxygen. As to the portion of oxygen which has disappeared, and which is not accounted for by the carbonic acid evolved, it may have combined partly with another portion of carbon, to form a limited amount of carbonic acid, which by the law of absorption is retained in the blood; and partly with hydrogen or some other oxidable constituent of the blood, without yielding a gaseous product.

These two experiments it will be observed point to exactly the same conclusions, and together with a number of others, where the mode of procedure was similar, and which were attended with similar results, have satisfied the author as to the fallacy of Magnus's doctrine, "that the oxygen received during respiration into the blood is kept there merely by the law of mechanical absorption, and enters into no chemical combination with that liquid." Had this assertion been well-founded, such a change as has been seen to occur, in the composition of the air enclosed along with blood, saturated as the blood already was with oxygen, could not have happened.

After having ascertained that air underwent certain changes in composition during its contact with blood, it next became an object to discover by which of the constituents of the blood these changes were induced. With this view the author successively subjected the organic compounds of the blood separately to the action of air, by a similar process to that adopted in the case of the blood itself.

A certain quantity of fresh fibrine, moistened with water, was saturated with oxygen, placed in a receiver along with eight volumes of air, and kept during twenty-four hours at a temperature of from 20° to 25° Cent. At the expiration of this time the gas on analysis was found to have the following composition:—

Oxygen	6·81	total oxygen = 17·98
Carbonic acid	11·17	
Nitrogen	82·02	
	100·00	

thus showing that fibrine takes up a certain quantity of oxygen, and gives off a stated amount of carbon combined with oxygen in form of carbonic acid gas.

The next experiments were made upon albumen, but as that substance could not be obtained in a pure, and at the same time uncoagulated state from blood, the albumen of the hen's egg was employed, which possesses very similar characters. It was found that when a certain quantity of the white of the hen's egg was well saturated with oxygen, and afterwards kept in contact with an equal volume of air during a certain number of hours at a temperature of 36° Cent., the gas on analysis gave in 100 parts,—

Oxygen	17·05
Carbonic acid	2·09
Nitrogen	80·86
	100·00

proving, in common with the experiments on the blood and on fibrine, that albumen also possesses the property of absorbing oxygen and disengaging carbonic acid.

Some comparative experiments were also made upon serum and upon blood-coagulum, in which it was found that the air confined along with the serum yielded on analysis—

Oxygen	16·74
Carbonic acid	2·30
Nitrogen	80·96
	100·00

while that confined with the coagulum contained—

Oxygen	8·57
Carbonic acid	7·29
Nitrogen	84·14
	100·00

It thus appears that the oxygen exerted a much more powerful action on the coagulum, which contained the fibrine and blood-corpuscles, than on the serum, which contained only albumen. The experiment thus corroborated the results previously obtained with pure fibrine and pure albumen. The pure fibrine was seen to produce a much greater change in the composition of the atmospheric air than the pure albumen from the hen's egg. The difference in the case of the coagulum and the serum was so much marked, that the author felt anxious to find out whence it proceeded; and under the impression that the hæmatine in the corpuscles might have mainly contributed to the result (as other organic colouring matters possess the property of absorbing oxygen and giving off carbonic acid gas), he took a small quantity of pure blood-hæmatine prepared by Verdeil's process, and put it into a vessel along with 1000 volumes of ordinary air. After the air had been kept in contact with the hæmatine for some months, the gas was analysed and found to contain—

Oxygen	16·01
Carbonic acid	3·80
Nitrogen	80·19
	100·00

The pure colouring principle of the blood, therefore, by exposure to ordinary air, gives off carbonic acid gas, and becomes oxidized in two ways; first by a loss of carbon, and secondly by direct combination with oxygen. The author considers that this last result furnishes additional evidence of the correctness of an opinion he hazarded two years ago*, imputing to the colouring matters of the vegetable and animal economy a more important office in the function of respiration than they before had been considered to possess, and regarding their principal function in organized beings as the absorbing of oxygen and exhaling of carbonic acid—a view altogether irrespective of Liebig's well-known hypothesis, which assigns the above office to the iron of the blood-hæmatine.

The author concludes by expressing the hope that his experiments will be considered as at least serving to establish one important fact respecting which further evidence was wanted, namely, that the entire volume of the respired oxygen is not transmitted in an uncombined state (as Magnus believes) to the various organs and tissues of the body, but that a portion of it enters into chemical combination with some of the organic constituents of the blood.

PATENT.

Patent granted to F. M. Jennings, *for Improvements in bleaching Vegetable Fibres.*

This invention consists in bleaching vegetable fibres in the state of cloth, thread, yarn, or as flax, hemp, jute, China grass, or cloths, known in the trade as unions (being mixtures of linen and cotton), or such like substances, in any state of preparation, or entirely unmanufactured, or as pulp, by the use of a solution of hypochlorite of soda, commonly called chloride of soda, in combination or admixture with an excess of caustic, carbonate, or bicarbonate of soda, or any mixture of those salts, or caustic, carbonate, or bicarbonate of potash, or any mixtures of those salts of potash and soda.

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* Verhand. Physik-Medizin. Gesellsch. zu Würzburg, Bd. v. 1854; and Erdmann's Journ. f. prakt. Chemie, Bd. lxiv. H. 5. 1855.

The patentee states that he is able to use chlorine in the state of combination or admixture with these substances at an earlier part of the process of bleaching than is now found to be either convenient or suitable in the present modes adopted for bleaching the above substances, especially in the case of heavy linens. He sometimes uses chlorides of the alkaline earths, in which instances he prefers employing a solution of caustic soda or potash, or a mixture of those alkalies, instead of using their carbonates, so as to prevent decomposition. In the place of hypochlorite of soda, hypochlorite of potash, or, as it is commonly called, chloride of potash, may be used when it can be obtained cheap enough. To bleach linen cloth, for example, according to this invention, it is soaked in water for a time, say twelve hours, or boiled in alkali, and then soaked in dilute acid. If lime be used, dilute muriatic acid is preferred, or the cloth is boiled in a solution of carbonate or caustic soda or potash, or mixtures of those substances, or a soap of oil, or grease, or rosin, as used at present in bleach-greens. If carbonate or caustic soda, or a mixture of those substances, be used, a solution of about 3 to 5 of Twaddle's hydrometer is preferred, and the cloth is boiled from four to six hours. The boiling is continued until the whole or greater part of the soluble portion of the colouring matter is dissolved in the common way, as at present in use. The linen cloth is then washed, and put into a solution of caustic carbonate or bicarbonate of potash or soda, or any mixtures of those salts. The patentee prefers the specific gravity of 1025, or 5 Twaddle's hydrometer, of carbonate of soda of commerce, as used by soap-makers or bleachers—slight impurities not affecting the result; and he adds a solution of chloride of soda of commerce, of such a strength that it would make the total solution of about from 1 to 2 Twaddle, calculating as if the above were water, or calculated, by adding in the chloride of soda, so as to increase the specific gravity by the addition of the chloride of soda. In this solution the linen cloth is placed and left for some hours; and suitable mechanical means being used to make the solution permeate, and cause fresh portions of the liquor to pass into and through the material, this operation may be brought to a close in about three or five hours, more or less. The linen cloth is next washed and soaked in dilute sulphuric or muriatic acid. The strength may be that generally used, about from 1010 to 1020 spec. grav., or from 2 to 4 of Twaddle's hydrometer. After this the linen cloth is washed in water and boiled in the usual way for from six to ten hours. It is then again put through the chloride and carbonate of soda solution (or whatever other solution is used), and washed, soaked in acid, and boiled as before described. These operations continue to alternate for about three, four, or five times, until the linen cloth assumes an appearance almost perfectly white.—Dated Feb. 5, 1856.

THE CHEMICAL GAZETTE.

No. CCCXL.—December 15, 1856.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Lithium and its Compounds. *By* L. Troost.

The author obtained a considerable quantity of lepidolite, from which he extracted 5 or 6 kilogrms. of carbonate of lithia. His experiments were made in the laboratory, and under the advice, of M. Sainte-Claire Deville.

The process employed by him is founded on the fact, that if a mixture of lepidolite and carbonate and sulphate of baryta be heated in a good furnace, the materials fuse and undergo a sort of liquefaction, which gives a perfectly fused but viscous glass at the bottom of the crucible, and above this a perfectly fluid portion, which may be removed from the crucible whilst hot either with an iron spoon or by decantation. This liquid on cooling forms a crystallized white mass, or one slightly rose-coloured by manganese. If the whole be allowed to cool in the crucible, it forms two solid, non-adherent masses. The white crystallized mass is a compound of sulphate of baryta and sulphate of potash with sulphate of lithia. The crystalline form of the sulphate of baryta predominates, to judge from the measurement of a single angle. Simple washing with boiling water separates the sulphate of baryta from the alkaline sulphates.

This process only succeeds with petalite by the addition of so much sulphate of potash or soda, that the total quantity of alkalies may be the same as in lepidolite. By increasing the quantity of alkalies in lepidolite, the amount of lithia obtained from it was also increased; the author obtained 3 per cent. Lime and sulphate of lime may be substituted for the carbonate and sulphate of baryta; and lime may be employed with chloride of calcium, but the volatility of chloride of lithium renders the sulphates preferable.

Lithium may be fused and poured in the air without tarnishing. It may be kept in a vessel filled with air. With potassium and sodium it forms alloys, some of which are lighter than naphtha.

The author first prepared this metal by a modification of the method of Bunsen and Matthiessen. He then tried to produce it by Sainte-Claire Deville's method for the preparation of sodium, but without success. By the action of sodium upon the chloride of lithium at a gentle heat, an alloy still containing much sodium is produced; to increase the proportion of lithium, the author immersed it in a glass of water with a surface-stratum of naphtha; the sodium decomposes the water before the lithium, and a globule is soon obtained which floats on the surface of the naphtha. This reaction shows that lithium departs from the alkaline metals, and approaches magnesium, the first metal which is prepared in this manner. The author has only obtained one oxide of lithium, which also establishes a relation between lithia and magnesia. The examination of the salts leads to the same conclusion. Whilst a current of carbonic acid diminishes the solubility of the carbonates of potash and soda by the formation of a bicarbonate, it considerably increases that of carbonate of lithia, like that of the carbonate of magnesia. Lithia does not appear to form a bisulphate or an alum. Chloride of lithium and nitrate of lithia are more deliquescent than the corresponding salts of magnesia; like these, they can crystallize with water of hydratation. At its temperature of fusion, chloride of lithium loses part of its chlorine and becomes alkaline, like chloride of magnesium. Salts of lithia do not furnish precipitates with carbonate of ammonia in presence of ammoniacal salts, and lithia forms double salts with the latter, like magnesia. Phosphate of lithia is insoluble, like that of magnesia, and the author considers the analogy between these two bases to be so close that the only means of separating them is the employment of caustic potash, which precipitates magnesia alone.—*Comptes Rendus*, Nov. 10, 1856, p. 921.

On Alloys of Aluminium. By H. Debray.

Aluminium forms alloys with most metals, and in most cases the combination takes place with great evolution of heat and light. An alloy of 10 parts of aluminium and 90 parts of copper possesses greater hardness than ordinary bronze, and is worked when hot with more ease than the best soft iron. As the proportion of aluminium increases, the alloys generally become harder; they become brittle beyond very narrow limits with gold and copper. These metals also lose their colour, and soon become completely colourless.

Aluminium becomes more brilliant and a little harder, still remaining malleable with small proportions of zinc, tin, gold, silver and platinum. Iron and copper do not greatly injure the properties of aluminium if they are not in too great quantities; 1 or 2 per cent. of sodium, on the contrary, forms an alloy which readily decomposes cold water.

For practical purposes, it is unnecessary that aluminium should be entirely deprived of iron. Metal reduced from impure chlorides, but of which the malleability and tenacity differed but little from those of pure aluminium, contained 7 to 8 per cent. of iron. The union of the two metals takes place with facility; the iron pokers with which the liquid baths are stirred in the furnaces where aluminium is produced become covered with a brilliant layer of this metal. Aluminium contaminated with iron is purified by a simple fusion in nitrate of potash.

The author alloyed 5 parts of aluminium with 95 parts of iron, without imparting to the latter properties very different from its own.

An alloy of zinc containing 97 of aluminium and 3 of zinc is a little harder than the metal, although very malleable; it is equal in brilliancy to any other alloy of aluminium. Aluminium may contain 10 per cent. of copper without losing its malleability, which is diminished, however; the metal reduced in copper trays contains from 5 to 6 per cent.; it is also worked with facility. Above 10 per cent. it becomes brittle, but remains white as long as the proportion of copper does not exceed 80 per cent. The alloy thus obtained is white and brittle, and resembles the metal of telescope-mirrors. The alloy with 85 per cent. of copper is still brittle, but begins to grow yellow. The copper probably loses its colour when it is below 82 per cent., which corresponds with $Cu^2 Al$.

The aluminium bronze already mentioned unites with the property of being forged when hot, that of great inalterability in presence of hydrosulphate of ammonia. Its yellow colour is fine, but inferior to that of the alloy of 95 copper and 5 aluminium.

An alloy of 3 parts silver and 97 aluminium has a very fine colour, and is unalterable in presence of sulphuretted hydrogen. 1 part of aluminium and 1 part of silver give a material as hard as bronze. An alloy of 99 gold and 1 aluminium is very hard, but malleable; its colour is that of green gold. The alloy of 10 aluminium is colourless, crystalline, and consequently brittle.—*Comptes Rendus*, Nov. 10, 1856, p. 925.

On the Behaviour of Iodide of Mercury to Ammonia, and a new Reaction for Ammonia. By JULIUS NESSLER.

[Concluded from page 453.]

Reaction for Ammonia.—Solution of iodide of potassium and iodide of mercury has long been employed as a reagent for the alkaloids, with which, even when greatly diluted, it gives a slightly coloured turbidity or precipitate. Fixed alkalies furnish no precipitate, and ammonia gives a crystalline precipitate only when greatly concentrated.

If however free potash be added to this solution, even traces of ammonia or of an ammoniacal salt produce a precipitate of the brown compound $NHg^4 I+2HO$, described on p. 450; and if more of the ammoniacal salt than can be decomposed by the free potash be added, the precipitate is dissolved, but is again precipitated by more potash. Iodide of potassium behaves in the same way, and dissolves the precipitate the more readily the less free potash is present. With a great excess of potash, none of the precipitate is taken up by iodide of potassium. To obtain a solution of the iodides of potassium and mercury free from excess of iodide of potassium, 20 grms. of the latter were dissolved in 50 cub. centims. of water, and iodide of mercury was added until some of it remained undissolved. The quantity of iodide of mercury added was 32·38 grms.; the portion remaining undissolved, when washed and dried, weighed 0·17 grm., so that 32·21 grms. were held in solution by 20 grms. of iodide of potassium. The compound HgI, KI requires 27·3 grms. of iodide of mercury to 20 grms. of iodide of potassium, so that more than an equivalent quantity of iodide of mercury dissolves in a concentrated solution of iodide of potassium at ordinary temperatures. When the solution was diluted to 200 cub. centims., a portion of the excess of iodide of mercury separated in fine quadratic octahedra. 20 cub. centims. of this solution were mixed with 30 cub. centims. of a concentrated solution of potash, and thus employed as a reagent for ammonia.

1 cub. centim. of liquid ammonia, containing 0·01 grm. of ammonia, was diluted to 10·000 cub. centims., and a few drops of this fluid, or at the utmost 0·0000005 grm., were sufficient to produce a yellow colour, and when slightly heated, a distinct precipitate in the reagent. A solution of chloride of ammonium, containing 0·000003 of the compound in the cubic centimetre, produced the same reaction. Ammonia could be clearly detected in rain-water collected upon an open space. This great sensibility is easily explained by the circumstance, that 17 parts by weight of ammonia are sufficient to produce a precipitate of 559 parts by weight, in accordance with the formula,—

$$4(HgI, KI)+3KO+NH^3=[NHg^4I+2HO]+7KI+KO.$$

Alkaline chlorides and oxysalts have no injurious influence upon the reaction; iodide of potassium is only injurious when sufficient caustic potash has not been added. The reaction is not produced in the presence of cyanide of potassium and sulphuret of potassium, even with concentrated ammonia and a great excess of potash.

Urea does not give the reaction in the cold, but probably by decomposition when heated. Ammonia cannot however be detected in this way in the urine, as a dark precipitate is usually formed on the addition of the reagent, independently of the ammonia.

Alkaloids behave towards this solution in the same way as towards pure solution of iodide of potassium and iodide of mercury, producing a white precipitate. Thus traces of ammonia may be detected in the presence of the volatile bases, conicine, nicotine, chinoline, aniline and æthylamine, which is of the more importance as ammonia usually makes its appearance during the preparation of these alkaloids; and they possess in common with it the property of forming clouds with vapours of muriatic acid, which has hitherto been the most delicate reaction for ammonia.

The whitish precipitate produced by solution of iodide of potassium and iodide of mercury in æthylamine and aniline, dissolves in an excess of the former, and is again thrown down by potash, producing a beautiful yellow colour with æthylamine. The precipitate formed in nicotine, coniine and chinoline, by solution of the iodides of potassium and mercury, dissolves with much greater difficulty in an excess, and is not again thrown down by potash.

Behaviour of the Ætherial Solution of the Compound NH^3, HgI *and* $NH^3 2HgI$, *with Fluids with an Alkaline Reaction.*—To prepare this fluid, the white body obtained by the action of liquid ammonia upon iodide of mercury was dissolved in æther, and the concentrated solution diluted with æther until a yellow stratum was no longer formed in a sample by the addition of water.

If this solution be mixed with a fluid which contains free fixed alkalies or alkaline earths, the latter becomes yellow, whilst the æther remains colourless.

Neutral carbonate of potash or soda gives the reaction like free alkalies, but weaker; and if they contain more than 1 equiv. of acid to 1 equiv. of base, the reaction does not take place. If solutions of alkaline bicarbonates be boiled for several hours, with replacement of the water volatilized, the monocarbonates remaining retain a sufficient excess of carbonic acid to destroy the reaction.

Dry bicarbonate of potash, heated for some hours to 446° F., and then dissolved, does not give rise to the reaction. The salt thus dried lost 4·32 per cent. more at 302° F., and then gave a yellow colour with the reagent; by calcination it lost a further 0·16 per cent.

To 27·6 cub. centims. (=4 equivs.) of a solution of this calcined salt, containing 0·01 grm. KO, CO^2 in the cubic centimetre, 0·25 cub. centim. of a solution of bicarbonate of potash, containing 0·01 grm. $KO, 2CO^2$ in the cubic centimetre, could be added, before a drop of it treated in a test-tube or small porcelain cup with the ætherial solution no longer became yellow. This 0·0025 grm. of bicarbonate of potash contained 0·00055 grm. more than 1 equiv. of carbonic acid, and this quantity is sufficient to prevent the reaction in 0·276 KO, CO^2. For 100 grms. KO, CO^2, 0·199 grm. CO^2 or 0·904 grm. $KO, 2CO^2, HO$ would be necessary.

Calcined carbonate of potash, left for twenty-four hours in a dry atmosphere of carbonic acid, did not take up sufficient of the latter to prevent the reaction; on the other hand, a solution of the calcined salt, after exposure to the air for twelve hours, no longer acquired a yellow colour.

To 10 cub. centims. of the above-mentioned solution of bicarbonate of potash, 4·7 cub. centims. of a solution of potash, containing 0·01 KO in the cubic centimetre, were added before a drop of it gave the yellow colour; thus 1 equiv. $KO, 2CO^2 HO$ required 1 equiv. KO. This reaction may perhaps be capable of employment in the volumetric determination both of the carbonic acid in bicarbonates and of the free alkalies. The experiments made with this view gave favourable results, but these were too few in number and made with the same fluids, so that no conclusion can be drawn as to the exactitude attainable with various degrees of concentration and under other conditions.

When bicarbonate of soda is heated to 230° F., a residue is left, the solution of which acquires a yellow colour with the reagent, but no longer gives the reaction on the addition of a little bicarbonate of potash.

The compounds of silica, alumina, and oxide of zinc with potash behave like free alkalies. In solution of biborate of soda of known strength, the reaction is only produced when rather more than 1 equiv. of a normal solution of potash has been added to 1 equiv. $NaO, 2BO^3$. A solution of freshly precipitated oxide of tin in potash did not give the reaction.

Ordinary phosphate of soda, $2NaO, HO, PO^5$, and the salt obtained from this by calcination, $2NaO, PO^5$, did not produce the reaction; to the former nearly ½ equiv. of potash could be added before the reaction occurred, but the solution of the latter acquired a fine yellow colour with far less potash; but if it be left long in contact with the potash the reaction does not take place.

Cyanide and sulphuret of potassium did not give the reaction; in the presence of free alkalies they prevent the reaction. If, besides free alkalies, a solution contains free ammonia, alkaline chlorides and alkaline earths, or their oxysalts, the reaction is not prevented, but it does not occur in the presence of iodide of potassium.

H. Rose divides the oxides by means of solution of bichloride of mercury into three groups, according to the greater or less strength of their basic properties. From the behaviour of the neutral potash-salts to turmeric and the above-described ætherial solution, the acids may be similarly divided into three groups. Thus,—

The neutral potash-salts of the acids of the first group do not give a brown colour to turmeric paper, or acquire a yellow colour with the ætherial solution.

Those of the second group give a brown colour to turmeric paper, but do not become yellow with the ætherial solution,—boracic acid, stannic acid.

Those of the third group colour turmeric paper brown, and acquire a yellow colour with the solution,—silica, alumina, oxide of zinc, phosphoric acid and carbonic acid.—Nessler's *Inaugural Dissertation, Freiburg im Breisgau*, 1856.

On some new Compounds of Cadmium. By Carl von Hauer.

The author has prepared a second compound of the chlorides of cadmium and nickel, belonging to the first group of the chloride of cadmium compounds established by him (see Chem Gaz. vol. xiii. p. 431). This is the double salt, $2NiCl+CdCl+12HO$, a salt which crystallizes in short, dark green, rhombic prisms, of remarkable beauty. It is easily obtained by bringing together the two constituents in the proportions corresponding with the formula, and allowing the solution to evaporate spontaneously. Analysis:—

Ni	17·72	2	= 59·2	17·97
Cd	16·98	1	56·0	17·00
Cl	31·78	3	106·2	32·24
HO	33·52	12	108·0	32·78

By leaving the aqueous solution of bromide of barium and bromide of cadmium to evaporate spontaneously, the author also obtained the

Double Bromide of Barium and Cadmium, $BaBr+CdBr+HO$, in large, colourless, shining crystals of the form of the corresponding chloride, $BaCl+CdCl+4HO$. Analysis:—

Ba	21·59	1	= 68·5	21·37
Cd	17·18	1	56·0	17·47
Br	50·43	2	160·0	49·92
HO	10·80	4	36·0	11·23

Sitzungsbericht der Akad. der Wiss. zu Wien, xx. p. 40.

ANALYTICAL CHEMISTRY.

New Method of determining Phosphoric Acid. By Dr. W. Knop.

The tedious operations of the ordinary methods of determining phosphoric acid are especially troublesome to those chemists who are engaged in agricultural, physiological, or pathological investigations, because in investigations of this nature we have almost always to do with materials containing phosphoric acid.

Impelled by the desire of discovering an advantageous process of analysis in the examination of ashes, milk, urine, manure, &c., especially for the interests of agricultural chemistry, I have endeavoured to found, upon the insolubility of the *phosphate of uranium and ammonia*, a salt which has hitherto probably been regarded as phosphate of uranium, a new method—

1. For the qualitative detection of phosphoric acid.
2. For its quantitative determination.
3. For effecting the analysis of bodies containing phosphoric acid in general.

On the addition of acetate of uranium to solutions of the soluble phosphates, strongly acidulated with acetic acid and heated, the latter immediately give a precipitate of phosphate of uranium. But if an ammoniacal salt be present in abundance in the solution, the precipitate also contains ammonia.

The insoluble salts of the bases ordinarily occurring with phosphoric acid are decomposed by boiling with acetate of uranium in the presence of ammoniacal salts and free acetic acid; the bases are dissolved.

The problem then was to adapt this behaviour to the establishment of an analytical method. In this paper I lay before chemists a first work upon this subject, in the hope that it may hereafter be completed by further observations. The analyses required for testing the accuracy of the method amount to a considerable number, in the execution of which M. Arendt of Frankfort willingly took part, as will be seen by the references to his analyses.

The analyses served for the solution of the following questions:—

1. What is the composition of the precipitate thrown down by

the addition of acetate of uranium to a fluid containing phosphoric acid, when the fluid contains an abundance of ammonia and free acetic acid?

Investigation.—The washed, yellowish-white precipitate, which has a tendency to pass into green, evolves ammonia slowly on the addition of potash, but very distinctly when heated in a glass tube.

A determination of the ammonia was effected by means of chloride of platinum. 1·066 of precipitate, dried at 212° F., was treated with a very little concentrated muriatic acid. To the perfectly clear solution 4 oz. of a mixture of equal quantities of æther and alcohol were added; to this chloride of platinum was added in excess, and the whole was left standing twelve hours. All the salt deposited upon the walls, consisting of chloride of platinum and ammonium, and subsequently separated phosphate of uranium, is scraped together into the fluid, and allowed to deposit afresh; the fluid is then decanted. The deposit is poured over first with a small quantity of concentrated muriatic acid, and then immediately with absolute alcohol, and directly afterwards put upon the filter. The filter is previously dried at 212° F., and weighed in a vessel capable of being closed. I obtained 0·366 of chloride of platinum and ammonium=4·0 of oxide of ammonium. This quantity is too small, but the experiment furnishes the positive proof that ammonia is contained in the precipitate. This was then determined as loss by calcination. In a series of experiments, 6 per cent. of loss were obtained; in two experiments, however, 9·8 and 9·6 per cent. Under certain circumstances, therefore, the precipitate probably contains water besides the oxide of ammonium.

0·738 of calcined precipitate gave further 0·235 of phosphate of ammonia and magnesia=0·1504 of phosphoric acid=20·4 per cent.

Thus we have—

		Calcined.		
U^2O^3	..	2 =	285·6	
PO^5	20·4	1	71·4	20·06

From this it appears that the precipitate, dried at 212° F., has the formula $(U^2O^3)^2+NH^4O+PO^5+xHO$, and that on calcination the ammonia and water are driven off, and there remains $(U^2O^3)^2+PO^5$. The precipitate therefore corresponds with the phosphate of ammonia and magnesia, which has hitherto been employed in the determination of phosphoric acid.

2. Has this precipitate the same composition under all circumstances? This question is answered both in a direct and indirect way.

The amount of phosphoric acid in a solution of phosphate of soda was determined by Arendt by the ordinary process.

10 cub. centims. of this solution gave—

$$\left.\begin{array}{l} a.\ 0{\cdot}1527 \\ b.\ 0{\cdot}1523 \\ c.\ 0{\cdot}1540 \end{array}\right\} \text{phosphate of ammonia and magnesia, or } 0{\cdot}096 \text{ phosphoric acid in 10 cub. centims. of fluid.}$$

Of this solution I employed each time 10 cub. centims., which were let out of a Mohr's stop-cock pipette—

I. By itself, only diluted with water.

II. With an addition of sulphate of magnesia and chloride of calcium.

III. With an addition of chloride of barium and carbonate of potash.

IV. With an addition of alum, magnesia and lime.

V. With an addition of perchloride of iron. After the addition, so much ammonia was added that the whole of the phosphate of iron was thrown down as a yellowish-white precipitate; the solution of uranium and acetic acid was then added in very great excess, and besides the muriate of ammonia produced, also an abundance of acetate of ammonia.

The solution I. gave 0·479 of calcined phosphate of uranium =0·096 of phosphoric acid. The others gave—

II.	III.	IV.	V.
0·471	0·475	0·477	0·483

All these precipitates were greenish by the reduction of oxide of uranium, which had resulted from calcination with the carbon of the filter.

I also determined the amount of phosphoric acid in dried phosphate of soda, the salt $(NaO)^2, HO+PO^5$.

I. 0·3 of this gave 0·726 of calcined phosphate of uranium=0·145 of phosphoric acid=48·3 per cent.

II. 0·5 gave 1·233 of calcined phosphate of uranium=0·246 of phosphoric acid=49·2 per cent. Thus we have—

	I.	II.			
NaO	..	..	2	= 62·4	
HO	..	..	1	9·0	
PO^5	48·3	49·2	1	71·4	50·0

I also determined the phosphoric acid in crystallized phosphate of potash. In this case a very great addition of muriate of ammonia is employed, as on account of the chemical similarity of potash and ammonia the precipitate might contain potash.

a. 0·585 crystallized phosphate of lime gave 1·472 of calcined phosphate of uranium=50·7 per cent.

b. 0·4875 crystallized phosphate of potash gave 1·31 of calcined phosphate of uranium=53·8 per cent.

	a.	*b.*		
KO	..	..	1	34·55
PO^5	50·3	53·8	1	52·27
HO	..	..	2	13·18

The analyses of the salts of soda and potash, the results of which are not very exact, presented the opportunity of finding the conditions under which the method becomes accurate and convenient.

With the first precipitates, the results of which agreed with those obtained in the determination as phosphate of ammonia and magnesia, I took the weight of the calcined precipitate as obtained when the filter upon which it is collected is burnt with the usual precautions, and did not oxidize the phosphate of uranium by the addition of nitric acid, although the greenish colour indicated a partial reduction. I soon found, in the progress of the investigation, that the reduction caused by the filter may be very considerable. Precipitates of 1·0 to 1·5 in weight may increase in weight 0·01 to 0·05, when, after the complete combustion of the filter, the precipitate is moistened with nitric acid and again calcined. It also appeared that the washing of the precipitate only takes place easily when its weight amounts at the utmost to 0·5, and it has been able to contract itself by long deposition. The precipitate of the second analysis of the potash-salt smelt distinctly of acetic acid when it was nearly dry; hence the excess; it evidently still contained acetate of potash.

These observations now led to the investigation of the conditions under which these inconveniences, proceeding from the slimy nature of the precipitate, disappear.

We deprive the precipitate of this slimy consistency by producing it in a porcelain dish, placing the dish containing it with the solution of the substances from which it has been deposited upon the sand-bath, until the precipitate with the other salts is brought to a state of dusty dryness, pouring strong acetic acid over the residue, and then boiling it with water for some time in order to dissolve the other salts completely. The precipitate is now pulverulent and heavy, so that it readily settles. By the employment of this process I obtained from 0·918 of phosphate of potash, 2·418 of calcined phosphate of uranium, which, after being once moistened with nitric acid, formed a beautiful egg-yellow mass in the crucible=0·483 of phosphoric acid, or 52·3 per cent. Thus,—found, 52·3; calculated, 52·27.

This determination consequently is as exact as can be desired.

The analyses necessary for the direct determination of the composition of the precipitates in the presence of bases were undertaken by Arendt. The following are the results:—

The solutions I. and II. contain only phosphate of soda, *no ammoniacal salt*; otherwise the process is as above. The solutions III. and IV. contained some muriate of ammonia; V. contained lime, baryta, magnesia and potash. All the precipitates obtained were decomposed according to the method described by H. Rose, by calcination with a mixture of cyanide of potassium and carbonate of soda; the phosphoric acid was determined in the solution obtained by lixiviation; and the uranium as protoperoxide by oxidation of the residue. By the analysis of the calcined phosphate of uranium Arendt obtained the following numbers:—

			$(MgO^2)^2PO^5$.	U^2O^3.
0·401	precipitate from solution	I.	gave 0·126	
0·977	... ...	II.	gave 0·306	0·765
0·457	... ...	III.	gave 0·143	
1·012	... ...	IV.	gave 0·323	0·787
1·538	... ...	V.	gave 0·499	1·193

These numbers lead to the following per-centages:—

	I.	II.	III.	IV.	V.			
Ur^2O^3	..	79·99	..	79·34	79·04	2	=285·6	79·94
PO^5	20·13	20·06	20·04	20·04	20·77	1	71·4	20·06

The analyses I. and II. prove that even when ammonia is excluded, the precipitate must still have the formula $(Ur^2O^3)^2+PO^5$ after calcination. It is convenient for the calculation that the percentage amount is so exactly 20 per cent.; we have therefore only to take the weight of the calcined precipitate moistened with nitric acid and again calcined, and divide it by 5 to obtain the phosphoric acid.

Every chemist knows how tedious the analyses are when phosphoric acid and alumina or iron occur together in a body. As it appeared, from the preceding trials, in which alum was added, that even the phosphate of alumina must be decomposed, I executed an analysis of phosphate of alumina.

A solution of alum was precipitated by phosphoric acid, and the precipitate completely washed and dried. The snow-white powder thus obtained dissolves at a boiling heat in much muriatic acid, forming a clear fluid, which on the addition of chloride of barium no longer gave any precipitate of sulphate of baryta.

A portion of the pure salt obtained was slightly calcined, weighed, and boiled with muriatic acid. The solution was mixed with muriate of ammonia, and then ammonia was added to it until it was completely filled with a precipitate of freshly precipitated phosphate of alumina. It was now boiled with a very great excess of acetic acid and acetate of uranium, and the fluid left to stand for some hours; the further process was as above described.

0·449 of pure phosphate of alumina gave 1·293 of calcined phosphate of uranium=0·2586 of phosphoric acid, or 57·5 per cent. The formula of the calcined phosphate of alumina is $Al^2O^3+PO^5$. We have therefore—

	Found.	Calculated.	
Al^2O^3	..	1	
PO^5	57·5	1	58·14

The difference between the amount of phosphoric acid found and calculated is only 0·9 per cent.

It may be cursorily mentioned, that in this analysis I also endeavoured to determine the alumina, by adding carbonate of ammonia to the fluid filtered from the phosphate of uranium. In this I did not succeed. I obtained an alumina containing uranium and a considerable loss of alumina.

The preceding analyses furnish us with the answers to the two principal questions which were obliged to be put before the method could be recommended for the separation of phosphoric acid. In what follows I shall describe the method itself more exactly:—

1. *Preparation of the Solution of Uranium.*—Pure oxide of uranium and ammonia or its carbonate is dissolved in an excess of acetic acid.

2. *Qualitative Testing of a Substance for Phosphoric Acid.*—The solution of the substance to be tested for phosphoric acid is mixed with ammonia as long as a precipitate makes its appearance, or, if earths or metallic oxides are absent in it, until it smells strongly of ammonia. Acetic acid is then added to it, and it is boiled in a small beaker or in a test-tube until the solution is clear. It is then removed from the heat, and a glass rod moistened with solution of acetate of uranium is immersed in it. If phosphoric acid be present, a yellowish-white cloud immediately proceeds from the immersed rod, and subsequently diffuses itself in the fluid. That there may be other acids which behave in the same way is a matter of course; the behaviour of the fixed acids, as compared with that of phosphoric acid, shall be examined hereafter.

3. *Quantitative Determination of Phosphoric Acid.*—The quantitative determination of phosphoric acid requires certain conditions:—

A. *The solution of the Substance.*—The substance whose amount of phosphoric acid is to be determined, and which must be freed from all intermixture of organic bodies, and especially from oxalic acid, by a preliminary calcination, is dissolved in muriatic or nitric acid, and concentrated as much as possible. The solution is saturated with ammonia. It is necessary that, besides the ammoniacal salts thus produced, and any that may have been added in case a solution originally neutral is mixed with muriate of ammonia, acetate of ammonia should be added. For with a great excess of free acetic acid, a portion of the mineral acid might otherwise be set free, which would dissolve the phosphate of uranium and ammonia. Acetic acid is then added in abundant excess.

The fluid thus treated contains all the salts in clear solution when alkalies, lime, baryta, and magnesia are present, and if iron be present, a precipitate of phosphate of iron. If alumina be present, a portion of it is dissolved and a portion undissolved.

The fluid is now mixed with acetate of uranium, whether a precipitate be present or not. If alumina or iron be present, the addition of acetic acid must be very large. The fluid is boiled or digested for a long time, when all the bases pass into solution; this is colourless, or brownish blood-red if it contains iron.

If the fluid in which the precipitate is produced be much diluted, or if only a small quantity of precipitate be obtained, the latter settles very well. If it can be allowed to stand quiet for twelve to twenty-four hours, the yellow fluid may be very completely decanted, or drawn off by a siphon. But in the presence of some salts, and especially of acetate of potash, the precipitate is deposited with difficulty, and as it is excessively fine it stops the filter. This is the case especially when the precipitate is obtained in quantities of more than 1 grm.

B. *Treatment of the Precipitate to render it capable of Filtration.*—The fluid in which the precipitate is produced is evaporated at first upon the sand-bath or over the smallest flame of a spirit-lamp, in the latter case with a large piece of wire-gauze laid under the dish, and finally on the water-bath, until it is perfectly dry. The residue is then treated with strong acetic acid, the dish is left standing for some time on the sand-bath; some water is then poured to it, it is heated nearly to boiling, and digested for some time.

The contents of the dish are then poured into a digesting glass, with the mouth broken off and ground obliquely to the longitudinal axis of the neck. Such glasses should be provided in sufficient numbers for determinations which so frequently occur. The precipitate is now poured entirely into the vessel. A film of the precipitate is often very firmly attached to the bottom of the dish. This is dissolved with a few drops of muriatic acid, and then saturated afresh with ammonia. This residue is also poured in, and the flask is filled up close to the lowest segment of its oblique orifice. Lastly, an oval piece of moistened Swedish filtering-paper is laid over the aperture, the flask is inverted over the filter, and left hanging quietly in the filtering stand. In suspending the flask over the filter, the aperture must first be introduced deeply into the filter, and the flask must afterwards be suspended somewhat higher as required.

In this way the washing of the precipitate is easily effected, whilst, when these precautions are not followed, it may be very tedious or even impossible. The precipitate lies deeply on the bottom of the filter, and when the first mother-liquor is filtered off from the upper part of the filter, the precipitate may be suspended and completely washed.

If a solution contains so much iron that on the neutralization of the mineral acid employed for its solution by ammonia the greater part of the phosphoric acid is combined with iron, so that the iron is thrown down as slightly coloured phosphate of iron, or as a brown precipitate from the intermixture of hydrated oxide of iron, the addition of the solution of acetate of uranium furnishes the precipitate of phosphate of uranium and ammonia in a remarkable modification. In this case, namely, it is at once dense, heavy and pulverulent, and washes admirably, so that there is no occasion for any further treatment of it. Here no water appears to be combined with the salt.

After the completion of the washing on the filter, the best form of which is the fan-shaped with numerous folds, the precipitate is completely dried.

C. *Combustion of the Filter.*—The crucible is put upon a quarter of a sheet of glazed paper, the filter is regularly introduced, ignited in the crucible, and allowed to smoulder away as much as possible. The precipitate must on no account be regularly wrapped up in the filter. The crucible must always be of sufficient size to allow the coal of the filter to stand in it surrounded by air, because by long contact with the coal of the filter without sufficient access of air, both oxide of uranium and phosphoric acid may be reduced, and phosphorus volatilized.

When the filter is completely burnt, the crucible is allowed to cool, and its greenish contents are moistened with nitric acid. At this time no more coal should be visible. It is dried over the smallest flame that can be produced by the large spirit-lamp and heated carefully, which may easily be effected, so that no decrepitation is heard and no spirting takes place. It is then calcined until the contents of the crucible no longer exhibit a white nucleus, and appear of a uniform egg-yellow throughout.

The precipitate now presents a constant weight after repeated calcination and weighing. In such weighings I have found that a reduction to protophosphate of uranium always takes place. By adding nitric acid and gently heating, an oxidation always takes place, which proceeds further spontaneously, when dense red vapours are evolved.

I may mention here particularly that I have convinced myself by experiment, that phosphorus may be volatilized by the action of carbon during calcination. A precipitate mixed with stearic acid gave a perceptible loss after calcination with the filter.

From what has gone before, I draw the conclusions,—

1. That this mode of determination of phosphoric acid presents this advantage over the other known methods, that the calcined precipitate has a constant composition. The phosphoric acid constitutes exactly one-fifth of the weight of the precipitate. The high atomic weight of the precipitate diminishes the errors of determination.

2. That phosphoric acid may be determined simply by acetate of uranium in the presence of those very bases from which we have most frequently to separate it, and the presence of which renders all the methods hitherto known very tedious.

3. That the method must cause a thorough improvement of the general process of analysis, as soon as we find out an exact mode of separating oxide of uranium from iron and alumina, because by it phosphoric acid may be entirely got rid of preliminarily from the analysis.

For after the removal of phosphoric acid, ammonia free from carbonic acid in most cases of analysis only throws down oxide of iron, alumina, and the excess of oxide of uranium added. We consequently obtain no division in the quantities of lime, magnesia, &c. present. The analysis must therefore be much more simple.

Even now this method affords facilities in the analysis of ashes, minerals, &c., if their constituents are not to be determined in one and the same portion. The improved instruments, which now furnish such excellent aids, allow of this being done.

If Mohr's stop-cock pipette be filled to 100 degrees with the solution of 2 grms. of the ash, and one portion be measured off for the determination for instance of the lime and magnesia, a second for that of the phosphoric acid, and so forth, the result of the endeavour after greater rapidity in the execution of analyses leaves little to be desired.

I hope soon to have the opportunity of making further observations in this direction. With regard to the examination of urine, however, I will here preliminarily mention a few facts which may be of use to physiologists and pathologists when they have to do with the determination of the phosphate of lime alone in the fluids of the organism.

If urine mixed with ammoniacal salts be precipitated directly with acetate of uranium, the expected precipitate is certainly obtained immediately, and even settles admirably, but nevertheless it is so slimy that it cannot be washed at all. It also contains intermixed organic substance, so that it acquires a dingy colour. Evaporation is here of little use, as the residue of the urine at last becomes very thick and syrupous.

Here, however, exact results may be obtained by mixing the urine, of which 80 to 100 cub. centims. are employed, first with an excess of chloride of magnesium or sulphate of magnesia and muriate of ammonia, and then, by the addition of ammonia, precipitating the phosphoric acid, combined with iron and the earths of the urine. This precipitate is not washed at all; it is burnt, without anything further, after drying, with an addition of nitrate of soda or ammonia, the residue is dissolved in muriatic acid, and the phosphoric acid is then determined in the solution thus obtained, and freed from all organic matters. As will be seen, this process does not exclude the determination of the lime by oxalic acid; and as, in many cases of disease, it is sufficient to know the amounts of lime and phosphoric acid, I think the process here described may be useful.

But probably we may also proceed in a much more simple manner. Thus if we add muriatic and acetic acids to a urine, and then a sufficient quantity of the solution of acetate of uranium, throw in cuttings of zinc foil, heat it until the zinc is briskly attacked, remove it from the fire, and let it stand until the zinc no longer effervesces briskly, and therefore until the muriatic acid is saturated, although the fluid is still acid with acetic acid, all the phosphoric acid is precipitated in combination with protoxide of uranium or perhaps protoperoxide. This green precipitate is dense and heavy, and may be easily washed. It is treated with nitric acid until all the uranium is again oxidized into peroxide, and then treated as already described, to obtain the phosphoric acid as phosphate of uranium.

In conclusion, it may also be mentioned that some experiments on the behaviour of the salts of protoxide of uranium have already been made in the course of this investigation in the laboratory of the Agricultural Experimental Station at Möckern, which has been for some time under my direction.

Arendt has found independently, by a treatment of the protophosphate of uranium, which is very insoluble in dilute muriatic acid, that this salt may be oxidized to perphosphate of uranium by means of hypermanganic acid, which may perhaps serve for a volumetric method for phosphoric acid.

On the other hand I have observed, as is stated above, that in the solution of perphosphate of uranium in muriatic acid the oxide-salt is reduced by zinc to phosphate of a lower oxide, either protoxide or protoperoxide, which is precipitated.

At the same time I have noticed that protoxide of uranium has very peculiar properities, as also appears from the investigations of Rammelsberg, Peligot, &c. Thus it seems to form combinations with ammonia, which belong to the remarkable series of the metallic ammonias (cobaltia, &c.).

I have already pointed out how important it will be to find a good method of separation for the mixture of alumina, oxide of iron and oxide of uranium, which is obtained in the employment of my method of separation, when the phosphoric acid is thrown down at the outset in the analysis of bodies which at the same time contain iron and alumina. Upon this problem I am already at work in common with Arendt. Even from the first experiments that we have made, it appears that this separation may be effected in two ways:—

1. By boiling the neutral acetic solutions of the mixture.
2. By precipitation with succinate or benzoate of ammonia from a neutral solution, or even from one mixed with an excess of carbonate of ammonia. The oxide of uranium is not thrown down by either of the organic acids, or rather the salts of oxide of uranium with these two acids are soluble in carbonate of ammonia.—*Chemisches Centralbl.*, Oct. 22, 1856, p. 769.

Method for the Detection of very small Quantities of Lead and Copper. By J. LÖWENTHAL.

The solution of the metal is evaporated to dryness, the residue is dissolved in 10 to 15 grms. of concentrated sulphuric acid by digestion on the sand-bath, and left to cool. The solution is poured into a test-tube, and from 5 to 8 drops of muriatic acid added to it. When lead and copper are present, a white turbidity is immediately produced. If the copper be in rather large proportion, the colour of the turbidity is not white, but yellowish-brown. By means of this method, 0·00001 grm. of lead and 0·000025 grm. of copper may be detected.—*Journ. für Prakt. Chem.*, lxvii. p. 878.

Testing of Woollen Tissues for intermixed Cotton.
By Dr. A. OVERBECK.

The tissue is laid in a solution of 1 part of alloxantine in 10 parts of water, pressed and dried. This process is repeated twice. It is then exposed to dry vapours of ammonia, and washed with distilled water. The woolly fibres are now permanently dyed crimson; the cotton fibres remain colourless.—*Archiv der Pharm.*, lxxxvii. p. 282.

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